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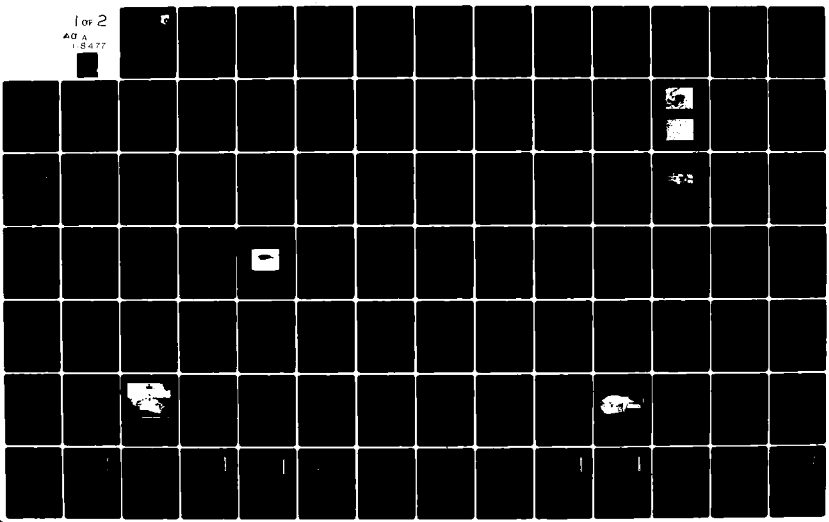

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OIL WEARMETAL ANALYSIS BY X-RAY (OWAX)

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MAY 1982

FINAL REPORT FOR PERIOD 1 SEPTEMBER 1980 - 15 FEBRUARY 1982

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A detailed feasibility study has been completed for application of the technique of x-ray fluorescence spectrometry to the analysis of wear metals in aircraft engine lubricants. Through laboratory experimentation, the relative values of various excitation methods, sample treatments, and sensor systems have been established. The recommended approach is based upon the modification of an existing portable x-ray analyzer to include a high-intensity x-ray excitation source, sample filtration, and a small computer for data analysis, display, and storage. For higher performance, the system incorporates a high-resolution

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detector (which must be cooled with liquid nitrogen prior to use) and a helium purge for the x-ray path. Elements within the required analysis range include Fe, Ti, Cu, Ni, Cr, Zn, and possibly Mg, Al, and Si. Because the x-ray approach emphasized particulates (retained by 0.4 micrometer filter), whereas the standard spectrometric procedure (SOAP) is much less sensitive to particles correlations between the two are found to be poor. Which method is superior for detecting incipient engine failures is unknown at this time since the appropriate parallel studies have never been conducted. A brassboard demonstration model of an OWAX unit (Oil Wearmetal Analysis by x-ray) has been built under a related effort.

FOREWORD

This report was prepared by Martin Marietta Corporation, P. O. Box 179, Denver CO 80201, under USAF Contract No. F33615-80-C-2071. The contract was initiated under Job Order Number SALMMEI1, "Oil Wear Metal Analysis by X-Ray". The effort was funded by San Antonio ALC/MMEI, Kelly AFB TX 78241, through MIPR FD2050-80-68046.

The Air Force Project Engineer was P. W. Centers (AFWAL/POSL). This technical report covers work performed from September 1980 to February 1982 by Martin Marietta Denver Aerospace.

This report was written by B. C. Clark and B. J. Cook. Major participants in the program were B. C. Clark, B. J. Cook, M. G. Thornton, and D. C. Van Hart.

Important additional contributions were made by C. O. Chen.

Development of the OWAX Brassboard was the result of the combined efforts of V. P. Woerdermann, B. C. Clark, M. G. Thornton, G. E. Hellewell, B. C. Cash, D. Wisherd, and L. G. Wolfert.

SUMMARY

The primary goal of this project has been to develop a concept for a portable wearmetal analyzer for aircraft turbine engine lubricants. Such a system will be particularly useful to the Air Force during rapid, temporary deployment of aircraft, as it will provide immediate analysis of wearmetal trends with no special operator training or extensive maintenance, and can be easily transported to sites which have no provision for oil analysis.

The initial approach for developing a portable oil analyzer was an evaluation of Martin Marietta's Portable X-ray Fluorescence Spectroscopy (PXRFS) unit for use with oil samples. This involved several theoretical studies, laboratory studies of actual oil samples, and other tests using standard solutions of metals in clean oil. In addition, a number of proposed modifications and improvements were thoroughly studied using special detectors, stimulus sources, and computer simulations.

To determine if the PXRFS concept was applicable to oil analysis, bulk samples of used oil were analyzed by pouring a small amount of oil into a sample cup and exposing the surface of the oil to x-ray irradiation. This method proved to be unsuitable, however, due to the fact that the metal concentration in less dirty oils was below the lower limit of detection for the PXRFS. Thus, methods for preconcentrating the wearmetals were investigated. The best procedure was found to be to prefilter the oil through 0.45 um membrane filters.

Choice of the prefiltration method led to the design of the Quantitative Filtration Apparatus (QFA). The QFA fits into the analysis unit, and automatically meters, vacuum filters, and provides a solvent rinse for each sample. All the operator need do is insert a clean filter (premounted in a 35 mm slide mount for cleanliness and ease of handling), lower the metering block by turning a knob, and add a small amount of oil. The QFA includes several "human-engineering" features designed to simplify operation and prevent inadvertent operator error.

Development of the QFA included testing to find the most effective solvent and the optimum filter. Ketones and xylenes were most compatible with synthetic oils and help dissolve the polymeric sludge which forms as the oil ages. For filtration, we chose Purolator Purpore's Tyrann-ME anisotropic membranes, as the anisotropic property gave the best filtration rate.

Further testing of the QFA included analysis of samples analyzed by SOAP, as well as standards of iron particles in clean oil. The calibration curve plotted from the iron standards data proved to be reliable, as are results of analyzing duplicate samples of the same oil. Correlation with the SOAP results was poor, however, apparently because of the fact that the SOAP procedure measures only the smallest particles and dissolved organometallic compounds, whereas the x-ray technique measures primarily particulates. In one case, a series of samples taken prior to mechanical failure showed essentially no wearmetals with the SOAP analysis, but significant concentrations when analyzed by x-rays.

To compliment the design of the QFA, an optimization study to choose the most appropriate radiation sources and detectors was conducted. Both radioisotope sources and several types of x-ray tubes were considered. A gold-targeted x-ray tube provides a short analysis time without excessively high voltage and, when coupled with a chromium-targeted tube, analyzes a wide range of elements.

The choice of a detector was made from several possibilities. The PXRFS uses a rugged proportional counter but, in so doing, sacrifices some resolution. A mercuric iodide ($Hg(I_2)$) detector provides greater resolution than the proportional counter, but is not yet commercially available. The silicon-lithium (Si(Li)) detector provides excellent resolution, but must be cryogenically cooled and laboratory models are bulky. However, portable Si(Li) detectors are now becoming available, and are recommended for the final design.

Trade-off studies led to the choice of a two-unit concept for the total system. The analysis unit, which filters and takes data for each sample, is coupled with a portable computer. The HP85 computer can analyze data, update

a file on each engine, and output an alert in the case of incipient engine failure. It also is intended to control the mechanics of analysis by regulating the vacuum pump, valves, and x-ray tube. By overlapping functions between the two boxes, analysis time is reduced to under four minutes per sample, with automatic tracking of each engine's history. The concept increases portability and economy, while minimizing maintenance. The only regular maintenance needed is occasional refilling of the solvent and nitrogen reservoirs, and emptying of the waste container.

In its recommended form, the OWAX system could provide rapid and simple analysis of aircraft engine oils without sacrificing the portability which is essential to deployment forces. Future studies could include comprehensive studies with respect to SOAP measurements and actual engine history to establish in greater detail the instrument's reliability in predicting abnormal wear and imminent engine failure.

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I. INTRODUCTION

The U.S. Air Force has an extensive program for systematic sampling and analysis of lubricants in aircraft engines. By monitoring the concentration of several key metallic elements for each aircraft engine, the sudden development of excessive engine wear can usually be spotted. Over the years, a large base of experience and data have allowed refinement of this methodology, so that in many cases even the specific fault within an engine can be diagnosed. Special maintenance can then make the necessary repair before a catastrophic failure occurs.

Two types of oil analysis equipment are currently operational: atomic emission spectrometry and atomic absorption spectrometry. The former are by far the more common. Both pieces of equipment are large, heavy, and relatively fragile. These factors greatly constrain their portability, yet the Air Force has need in certain cases to transport such equipment for support of deployed forces. For this reason, the development of new instrumentation which is lightweight, compact, and rugged is being pursued.

Martin Marietta Denver Aerospace has developed a battery-operated Portable X-ray Fluorescence Spectrometer (PXRFS) for use in elemental analysis in remote locations. The objective of this study has been to determine the feasibility of suitably modifying this instrument to provide a transportable oil wearmetal analyzer based upon the principles of x-ray fluorescence.

To help guide the direction of this study, a set of "desirable goals" were established. These design criteria were not to be interpreted as unmutable requirements, but rather as a group of system optimization objectives. They are:

a. Portable instrumentation weight under 50 pounds (22.7kg).

b. Simple, reliable, and maintainable instrumentation.

c. Analytical capability of 150 samples per 8-hour period.

d. Simple operational procedures and minimum sample handling.

e. Printed record of results on each sample coupled with sufficient data storage and retrieval capability to provide automatic data evaluation based on prior 5 samples from same unit.

f. Special sample treatment may be used if simple, safe, and economical to implement.

g. Analysis is to be wearmetal particle size-independent.

h. Instrumental cost per unit is not to exceed $35,000 each.

i. Multi-element single operation analysis is required. Elemental capability is Fe, Ag, Ti, Al, Cr, Mg, Si, Mo, and Ni (also Cu).

j. Accuracy and repeatability are to be equal to or exceed SOAP instrumental capabilities.

k. Power requirements are to be compatible with power availability (120 VAC, 50-60-400 Hertz; 220-240 VAC, 50-60-400 Hertz.

l. Type II, Class 4, Style B of MIL-T-28800B is to be considered.

II. TECHNICAL STUDIES

In the sections which follow, we report on a number of laboratory experiments, engineering analyses, and system trade-off studies performed as the technical basis for this report. In the last section, the overall feasibility of candidate x-ray oil wearmetal analysis instruments are discussed.

1. Performance of the Portable X-ray Fluorescence Spectrometer

Background

To perform geochemical analyses aboard the Viking lander on Mars, Martin Marietta designed a highly miniaturized, low-power-consuming x-ray fluorescence system. It used radioisotope x-ray sources instead of an x-ray tube for exciting the fluorescence, and rugged miniature proportional counter tubes to detect x-rays and produce output pulse amplitudes proportional to x-ray energies. This highly successful instrument obtained detailed analyses of two dozen soil and duricrust samples at the two Viking landing sites on Mars.

The X-Ray Fluorescence Technique

X-ray fluorescence is a commonly used laboratory method for determining the elemental composition of samples. Typically, an x-ray source irradiates the sample, producing emission from the sample of fluorescent x-rays at discrete energies characteristic of the chemical elements in the sample. The emitted fluorescent x-rays are then analyzed by an energy-sensitive detector.

The geometrical arrangement can be seen in Figure 1-1. None of the angles or distances are critical, but for best analytical accuracy they should be kept constant. Certain other factors of geometry are important to minimize the amount of scattered radiation reaching the detector; collimators are used with both source and detectors for this purpose. The materials used in the collimators and sample holder must be given careful consideration to prevent interfering secondary fluorescences. Even trace elements in these materials can affect the performance of the system.

The radiation source to excite the sample can be any radiation capable of ionizing atoms, preferably with sufficient energy to ionize K and/or L shell electrons. The sources most useful for the oil-wearmetal analysis application are certain radioisotopes and x-ray tubes.

X-RAY FLUORESCENCE TECHNIQUE

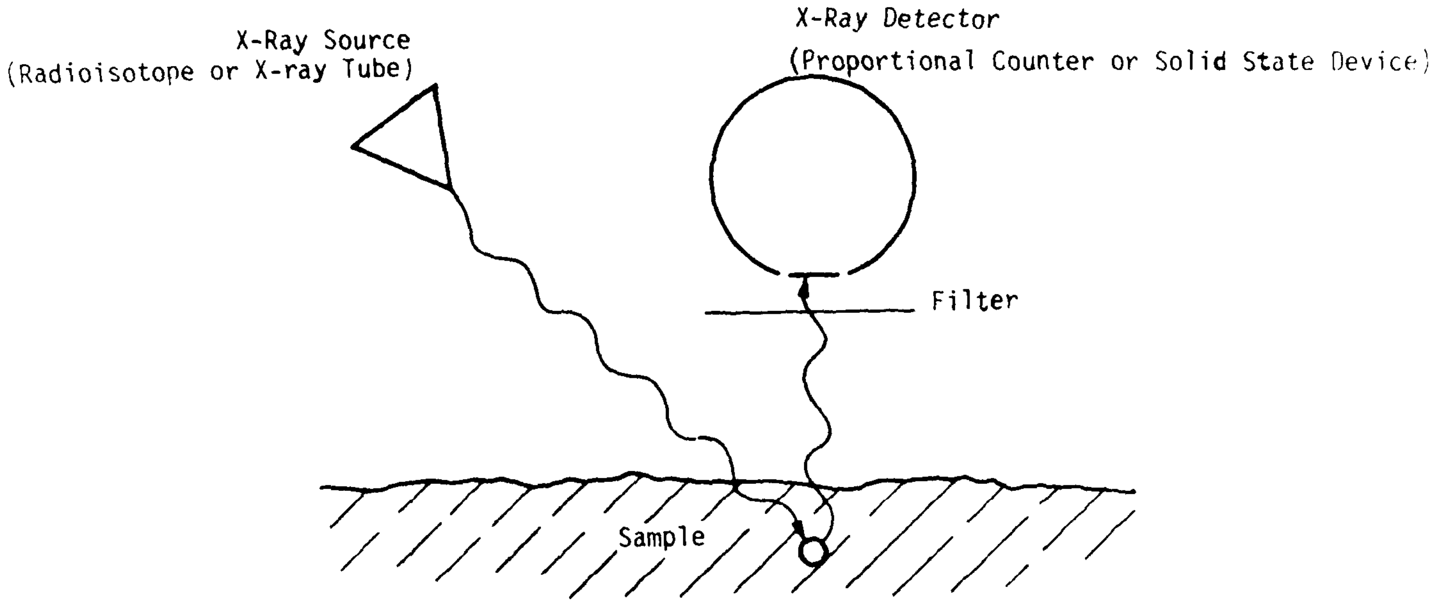


Figure 1-1

X-Ray Fluorescence Technique

The detector used in x-ray fluorescence may also be one of several different types. It must be capable of absorbing the fluorescent x-rays and measuring their energy. Of the different detectors available, some have much higher resolution than others. By resolution, we mean the ability of the detector to distinguish between two x-rays which have only slightly different energy. If the energy resolution of the detector is poor, then peaks from the two x-rays will overlap and it will be difficult to detect one of the x-ray's energies if the other energy is at a much greater intensity. Thus, if we have a very high concentration of iron in a sample, which produces x-rays at an energy of 6.40 keV, but a lower concentration of nickel, with fluorescent x-ray at 7.48 keV, we find obscuring of the nickel in the spectrum produced by a low-resolution detector such as a proportional counter; whereas the x-ray from zinc (8.64 keV) may be clearly distinguished. In Section 2 below we give examples of the differences in results between lower and higher resolution detectors.

Portable X-Ray Fluorescence Spectrometer (PXRFS)

The technology used for the Viking x-ray fluorescence geochemical analyzer was applied to develop a small portable x-ray fluorescence spectrometer for both field and laboratory use. Specific improvements included self-contained power, oscilloscope and liquid crystal readout capabilities, and a multi-channel pulse-height spectrum analyzer for quick analyses.

Specifications of this unit may be seen in Table 1-I. The unit is pictured in Figure 1-2.

Bulk Oil Analyses with PXRFS

A number of standardized oil samples ("Conostan standards") were obtained from the JOAP Office at the Pensacola Naval Air Station. These standards contain organometallic compounds at levels equivalent to precise parts-per-million (PPM) concentrations of various metallic elements.

TABLE 1-I

PORTABLE X-RAY FLUORESCENCE SPECTROMETER

Weight: 16 pounds (includes main unit, sensor head, and batteries)

Battery life:	data acquisition mode	7 hours
	display mode	13 hours
	"asleep" mode	60 hours

Note: Times quoted are for rechargeable NICad batteries. With higher power density (non-rechargeable) batteries, such as the lithium type, operating times are up to 10 x longer.

Dimensions:	Total unit (with Sensor head stowed):	11 x 11 x 5"
	Sensor head alone:	10.5 x 2.5 x 1.5"
	Main unit alone:	11 x 8 x 5"

Volume: less than 0.5 cubic ft.

Sensor cable length: 4 ft.

Standard samples: 2 internal, 11 external

Electronics: Low-power CMOS, including RCA 1802 microprocessor. 1024 channels x 16 bit pulse-height analyzer (divisible by 2) 32 kbit EPROM for operating program and data base Liquid-crystal display (LCD) with 6 alphanumeric characters. Cathode ray tube (CRT) for spectrum display internal clock; automatic power-saving switching Analog plot output: tape recorder output (optional) Spectrum cursor for peak identification and ration calculations, with dual display for L lines.

Radiation Sources: Fe-55 at 100 mCi; half-life - 2.6 yr.; 5.9 keV
Cd-109 at 15 mCi; half-life - 1.2 yr.; 2.2 keV

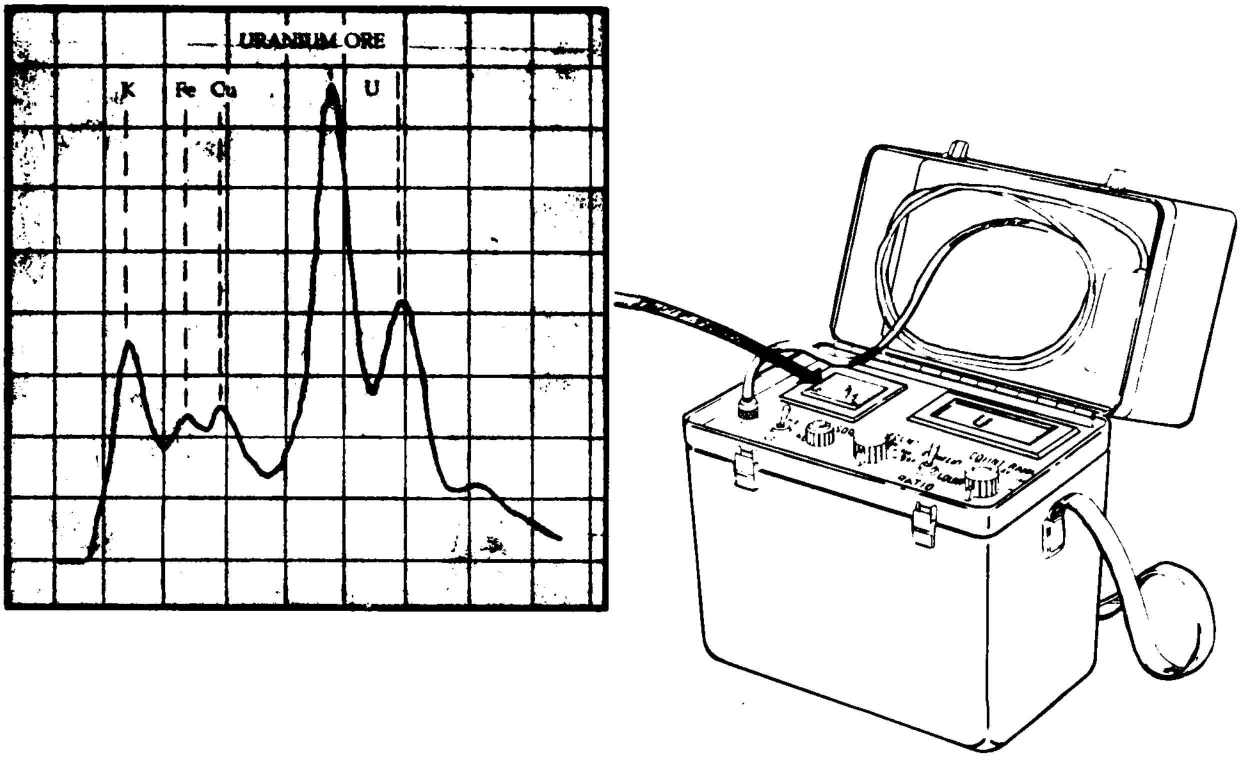


Figure 1-2
Portable X-Ray Fluorescence Spectrometer

Aliquots of oil were taken from these samples, placed into Spex sample cups, covered with a 0.25 mil Mylar foil, inverted, and positioned over the analysis port of the PXRFS sensor head. The results of this series of measurements clearly indicated two problems: (1) loss of adequate sensitivity for many elements below a concentration of 30 ppm, and (2) overlap interference between some elements of the limited resolution of the proportional counter detectors and the strong backscatter signal from oil molecules.

An example is the spectrum of Figure 1-3, which is for an oil standard containing 100 ppm each of such elements as Ti, Cr, Fe, Ni, Cu, Zn, Pb, and Mo. The excitation source is a Cd-109 isotope source. It can be seen by inspection of this spectrum that elements such as Fe, Ca, Pb, and Mo are readily detected (the peak B1 is the Cd-109 backscatter signal). However, bunching occurs in the Ni-Cu-Zn region, which means that computer deconvolution of the spectrum would be required to determine the levels of each of these elements. Low levels of any one of these three would be difficult to resolve.

Similar measurements on actual used engine oil samples produced the same general results. Previous studies with water pollution samples in our laboratory had shown that extremely large gains in detection sensitivity can be made if the pollutant elements are precipitated onto a filter and the water removed before the x-ray fluorescence analysis. Figure 1-4 shows one such example, where the filter precipitate is only 30 micrograms gram (30 ug) of lead (Pb). This corresponds to a sensitivity of considerably better than 0.1 ppm of Pb in a 300 milliliter water sample. It was therefore decided to try to detect wear-metals captured by filtering small quantities of oil through a suitable filter. This approach was successful and resulted in detectable x-ray fluorescence signals from wearmetals. Several studies were conducted with the Scanning Electron Microscope (SEM) to investigate the size distribution and morphology of the trapped wearmetal particles. From this approach, it was discovered that besides retention of discrete particles which are larger than the filter pore size, Figure 1-5, there is also retention of a very considerable amount of organic degradation product (sludge, ploymud,

D20-100

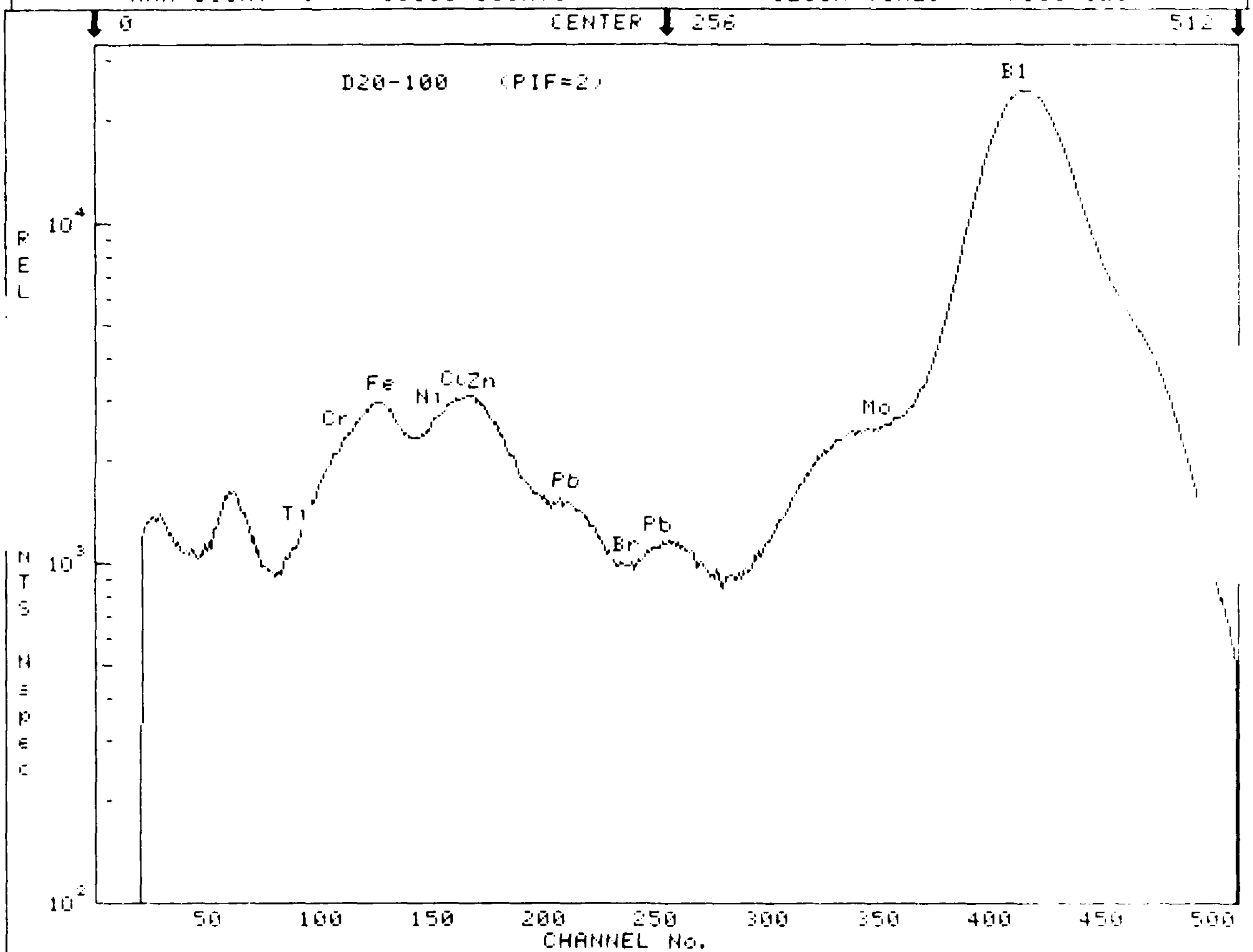
PC-4 Cd-109 RunID: OW-1

STORED UNDER: SPCF08
SPECTRUM #: 2
CHANNELS : 512
OFFSET : 0

OPERATOR: DVH
START : 13:53:30
DATE TAPED: 5580

TOTAL COUNT: 3577323 COUNTS
INTEGRATE PEAK: 0 COUNTS
MAX COUNT : 31335 COUNTS

COUNT RATE: 503.5 CPS
LIVE TIME : 0 SEC
CLOCK TIME: 7105 SEC



COMMENTS TO DATE

JOAP Oil Sample.

Figure 1-3
Bulk Oil Spectrum Taken With PXRFS

Pb 30ug (MM-412)

PC-4 Cd-109 RunID: WS-243

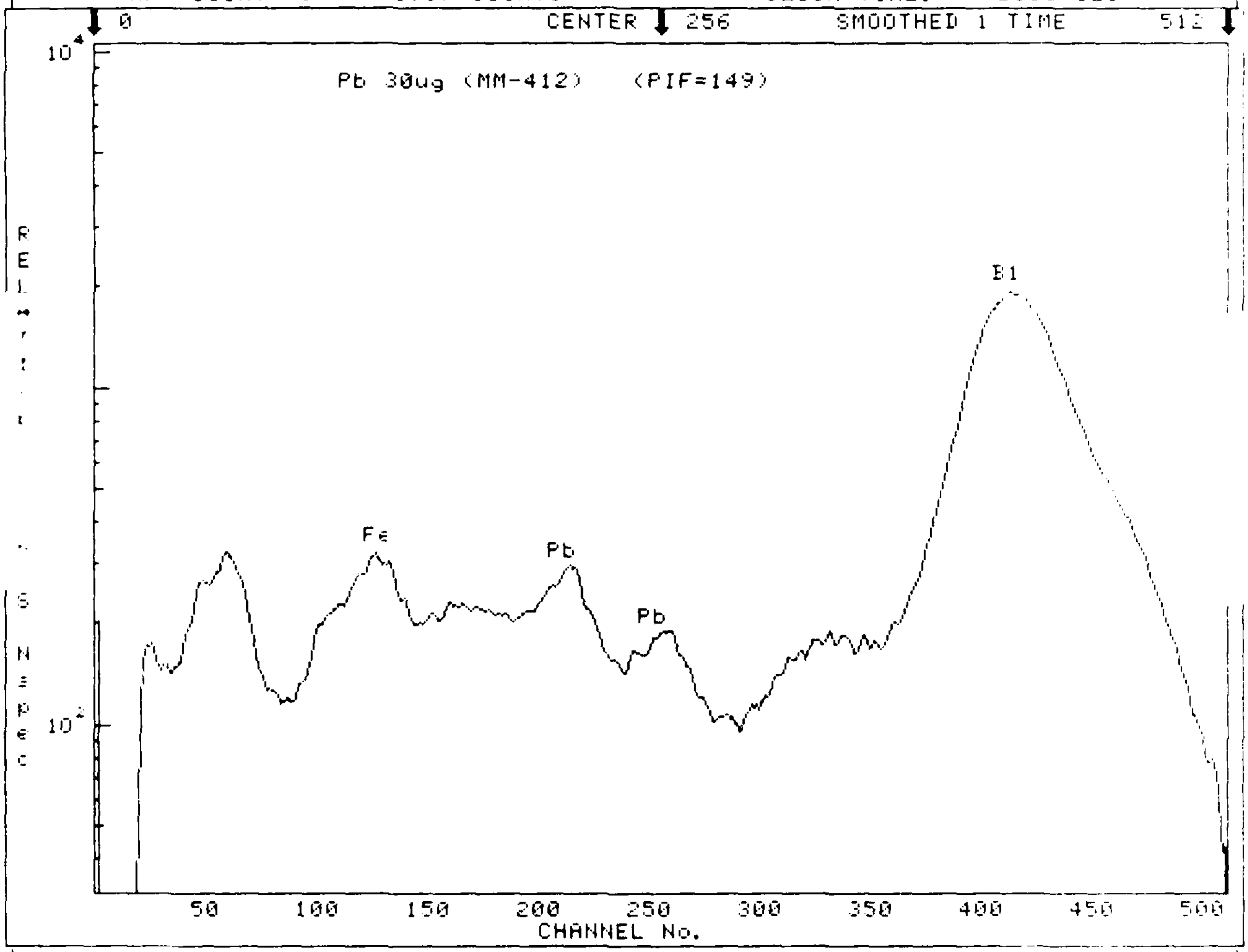
STORED UNDER:SPCF03

SPECTRUM #: 149
CHANNELS : 512
OFFSET : 0

OPERATOR: DVH
START : 12:43:42
DATE TAPED: 5980

TOTAL COUNT: 172021 COUNTS
INTEGRATE PEAK: 0 COUNTS
MAX COUNT : 1917 COUNTS

COUNT RATE: 86.0 CPS
LIVE TIME : 0 SEC
CLOCK TIME: 2000 SEC



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PC-4 in air. Sample in cup. Repeated spectrum. 86 cps.

Figure 1-4
Spectrum of 30 ug Pb
Preconcentrated on Filter

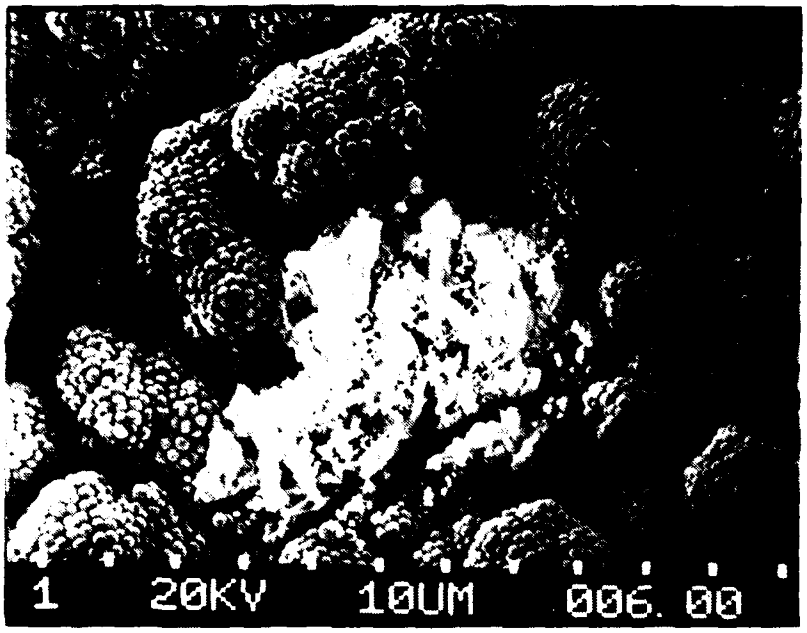

Figure 1-5
Scanning Electron Microscope (SEM): Discrete Particle Retention

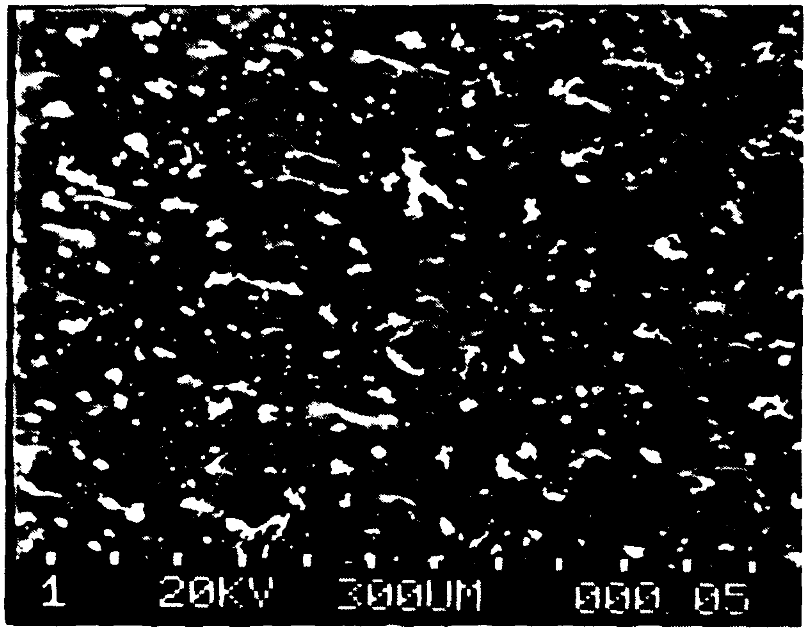

Figure 1-6
SEM: Retention of Organic Degradation Product

etc.), Figure 1-6. This organic matter apparently contains many very fine particles which, if free, could pass through the filter. The sludge may also contain organometallic molecules formed in the oil during engine wear. Thus, not only are discrete metallic particles greater than 0.4 micrometers (um) (a typical pore size) retained but a representative fraction of the smaller particles, including some "dissolved" metal, are retained as well. During this study, over 30 samples of used engine oils were used in filtration tests; in not a single case did any of these filter samples fail to contain measureable quantities of one or more wearmetal elements. A typical example of a filtered sample measured by a PXRFS detector (proportional counter) is that of sample JOAP-10, shown in Figure 1-7. Here, the important contributors to the observed spectrum are the signals from chromium (Cr), iron (Fe), and copper (Cu) wearmetal debris.

Sections 5 and 6 below discuss in greater detail the results of various tests with filtration methods. In the following paragraphs, the important considerations of wearmetal particle size dependency of x-ray fluorescence and other analytical measuring techniques are examined.

Particle Effects

The sizes and morphology of metal particles produced during primary wear is dependent upon the physical mechanism which produces the wear. Such mechanisms may be classified many different ways, but for purposes of summarizing some of the literature data on particle sizes, we provide Table 1-II. The major points are that the morphologies run the gamut of sharp and angular, to equiangular (approximately cubical) to perfectly spherical. By far the most common are apparently irregular particles with aspect ratios of two to ten. Primary wear fragments have characteristic particle sizes of micrometers to tens of micrometers. Subsequent grinding action of contacting surfaces within the engine will reduce the particles to small sizes, with attendant secondary wear of engine parts.

It is well known that the two present techniques used in the Spectrometric Oil Analysis Program (SOAP) are sensitive to dissolved metal and sub-micron particles, but have very poor sensitivity for most primary wear particles. As seen from Figure 1-8, which is adapted from the publication by Brown*,

```
        PC-4        Cd-109        RunID: OW-5
STORED UNDER:SPF08D
SPECTRUM #:     39                OPERATOR: bjc
CHANNELS   :   512                START    : 10:28:24
OFFSET     :     0                DATE TAPED: 1125 81
      TOTAL COUNT:   70419 COUNTS    COUNT RATE:    352.1 CPS
  INTEGRATE PEAK:       0 COUNTS    LIVE TIME :        0 SEC
      MAX COUNT  :     673 COUNTS    CLOCK TIME:      200 SEC
0              CENTER 256       SMOOTHED 2 TIMES        512
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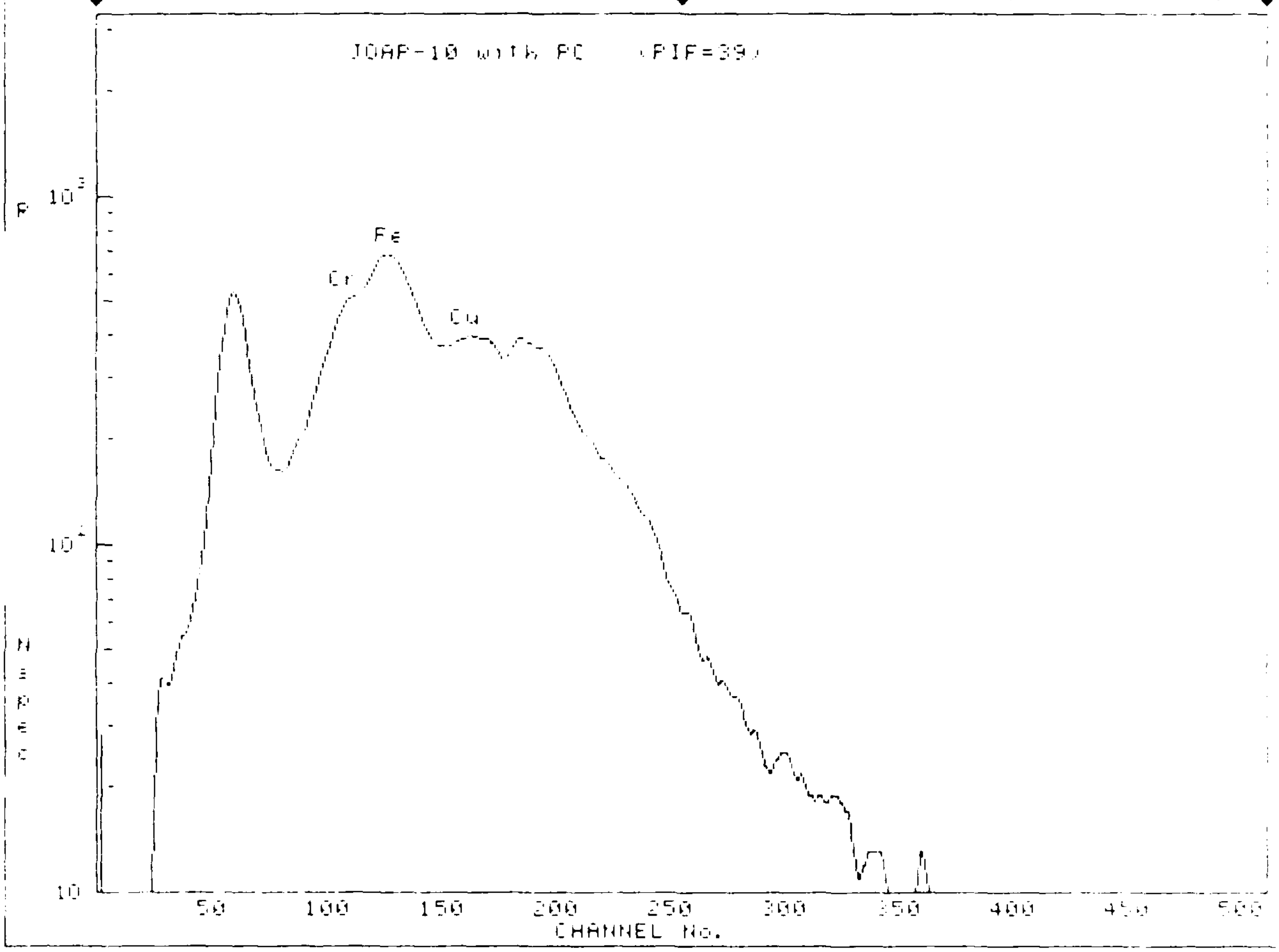

COMMENTS TO DATE

3.5 ml oil on 0.45um Tyranm. With proportional counter, Au -ra tube, In air

Figure 1-7
Preconcentrated Oil Wearmetals
Measured by PXRFS Proportional Counter

WEAR

TYPES	PARTICLES	
ADHESION	NORMAL RUBBING	(1 x 5 UM)
ABRASION	SPALLS	(2 x 20 UM)
	SPHERES	(1 - 10 UM)
SURFACE FATIGUE	CUTTING FRAGMENTS	
CORROSION	SEVERE	(30 UM)
	SUBMICRON	

". . . WEAR MODES SUCH AS SPALLING, OR EXCESSIVE ABRASION OR CUTTING WEAR, GENERATE PRIMARY PARTICLES WELL IN EXCESS OF 5 MICRONS." (L. LEONARD, JOURNAL OF LUBRICATION TECHNOLOGY, APRIL, 1977.)

MARTIN MARIETTA

Table 1-II
Wear

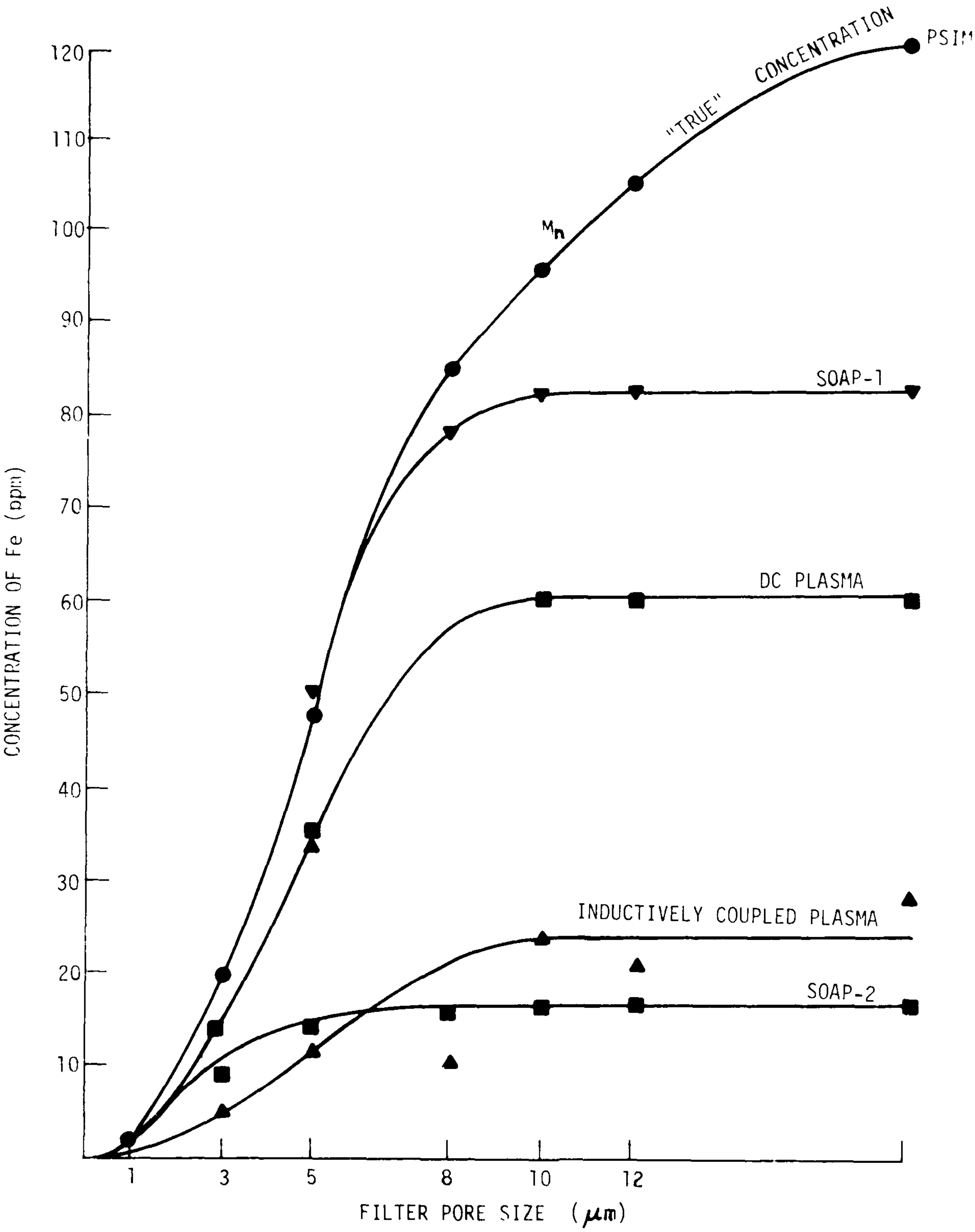

Figure 1-8
Particle Size Dependent Analysis of Fe

et.al., the less common atomic absorption instrument (SOAP-2) deviates from the "true" curve at particle sizes greater than about 2 um, while the rotating disk anode emission spectrometer instrument (SOAP-1) begins losing sensitivity for particles greater than about 6 micrometers.

The sensitivity of x-ray fluorescence to different particle sizes can be calculated for specific sizes and shapes in a straight-forward manner, unlike analytical methods in which complex sample viscosity and/or volatility factors affect the loss of particles from the analysis volume.

Fluorescent x-rays emitted from a particle are attenuated by the portion of the particle through which they must pass in order to reach the detector. Under most operating scenarios, the incoming x-ray which excites the fluorescent emission has greater penetrating power than the secondary. As examples of fluorescent x-ray attenuation, pure iron and pure titanium x-rays are essentially transparent to their own x-rays for particle diameters less than 1 um. Less than half of the fluorescent x-ray emission is lost to self-absorption for particle thicknesses of 10 um. At about 30 um thickness, the emission intensity is still 20% of the surface intensity.

A computer program (PARTEM) has been written to calculate the detailed "particle emission" as a function of particle thickness, composition, fluorescent x-ray energy, and energy of the excitation source. This calculation uses the physics of x-ray interaction and a data set of highly accurate fundamental constants and interaction cross-sections. Some results are plotted in Figure 1-9. Because of the energy of the excitation radiation (L-alpha line from gold-targeted x-ray tube), Ti becomes even less particle-size dependent than Fe. This is because the mass absorption coefficients for the excitation and emission energies are more equal in this case than for Fe or Cu matrices. In the calculation, the particles are modeled as being cubical in shape. More realistically, the particles are quite angular. AS our SEM photographs have clearly shown, the

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*J. R. Brown, C. S. Saba, W. E. Rhine, K. J. Eisentraut, Analytical Chemistry 52, 2365 (1980).

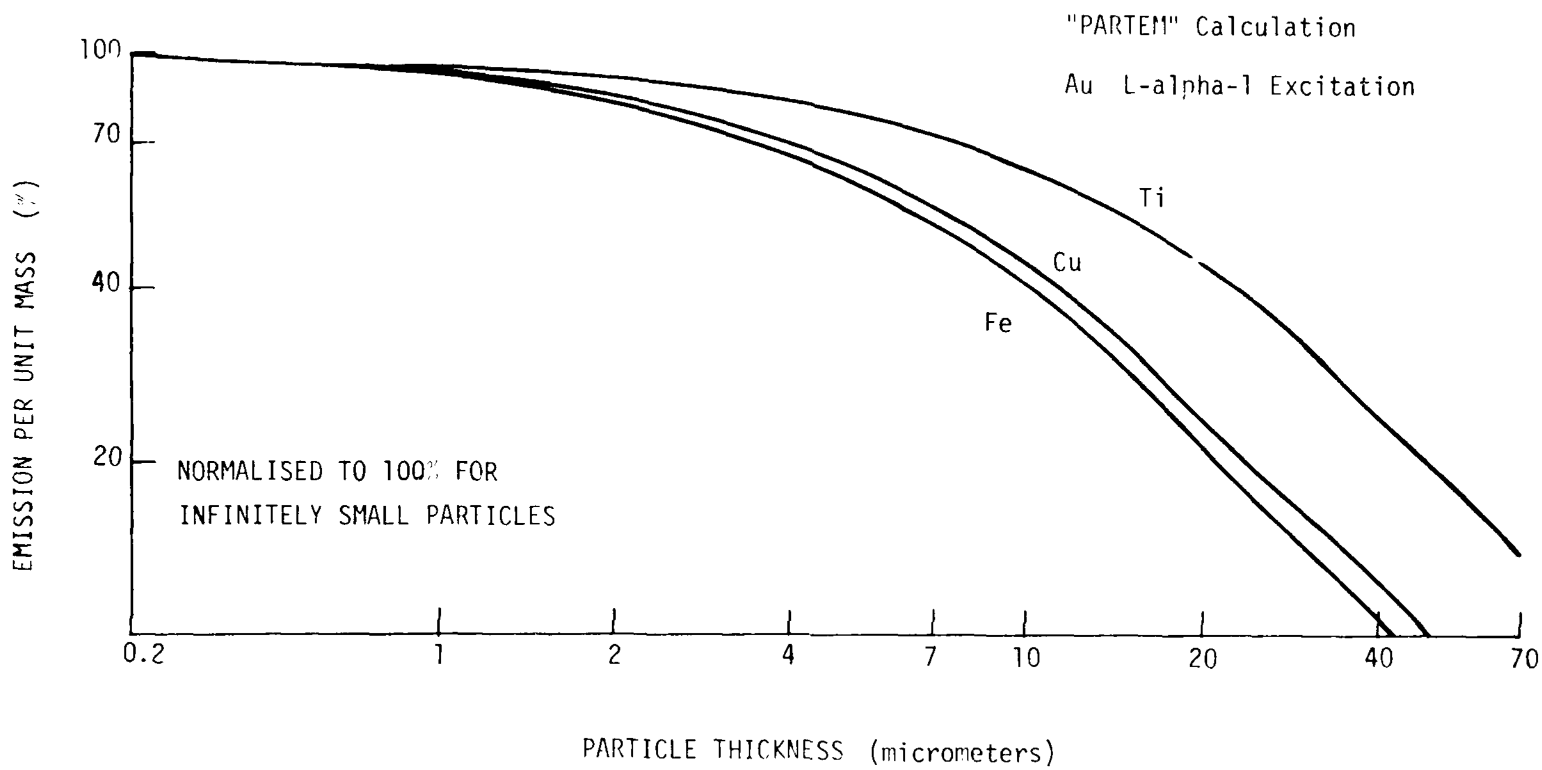


Figure 1-9
Sensitivity of X-Ray to Cubical Particles

hydrodynamic forces involved in the filtration step are very effective in "plating out" the particles so that their minimum thickness will normally be presented toward the x-ray beam, Figure 1-10. Thus, in practice, if a filtration technique is used, the x-ray fluorescence should be even less particle size dependent than the curves of Figure 1-9 might indicate. In a bulk analysis, the particles will tumble due to Brownian motion or agitation of the sample. But in the bulk case also, the curves of Figure 1-9 are a worst case limit since the maximum area exposed to the x-ray beam is that with the minimum thickness in the beam.

2. High Resolution Detectors

The chief advantage of higher resolution detectors is restriction of the signal to a narrower energy width, which allows better detectability of low concentrations of an element in the presence of other elements. The disadvantages of higher resolution detectors include cost and certain operational considerations.

Three types of detectors are applicable to the oil wearmetals analysis problem: the miniature proportional counter (PC), the mercuric iodide solid state detector (HgI_2), and the silicon solid state detector Si(Li). As shown in Table 2-I, there is about a factor of three improvement in resolution for each step that one moves up this sequence. Comparisons of two of these detectors are shown in Figures 2-1 and 2-2. In the first figure, the zinc sample of 10 micrograms of powder is readily detected by both sensors. However, the peak in the Si(Li) detector output is much sharper, in accordance with its much higher resolution. An appreciation of the value of this improvement can be obtained from inspection of the second figure (2-2) where two spectra from the 300 ppm Conostan standard are overlaid. Whereas the PC detector spectrum includes composite peaks of several elements, the Si(Li) detector is capable of cleanly resolving all elements within the excitation energy range. Which detector is required depends upon the characteristics of the sample, including which specific metals are present and what their concentrations are relative to one another. In the following sections, we examine the characteristics of the higher resolution detectors and compare their performance with the baseline proportional counter detector.

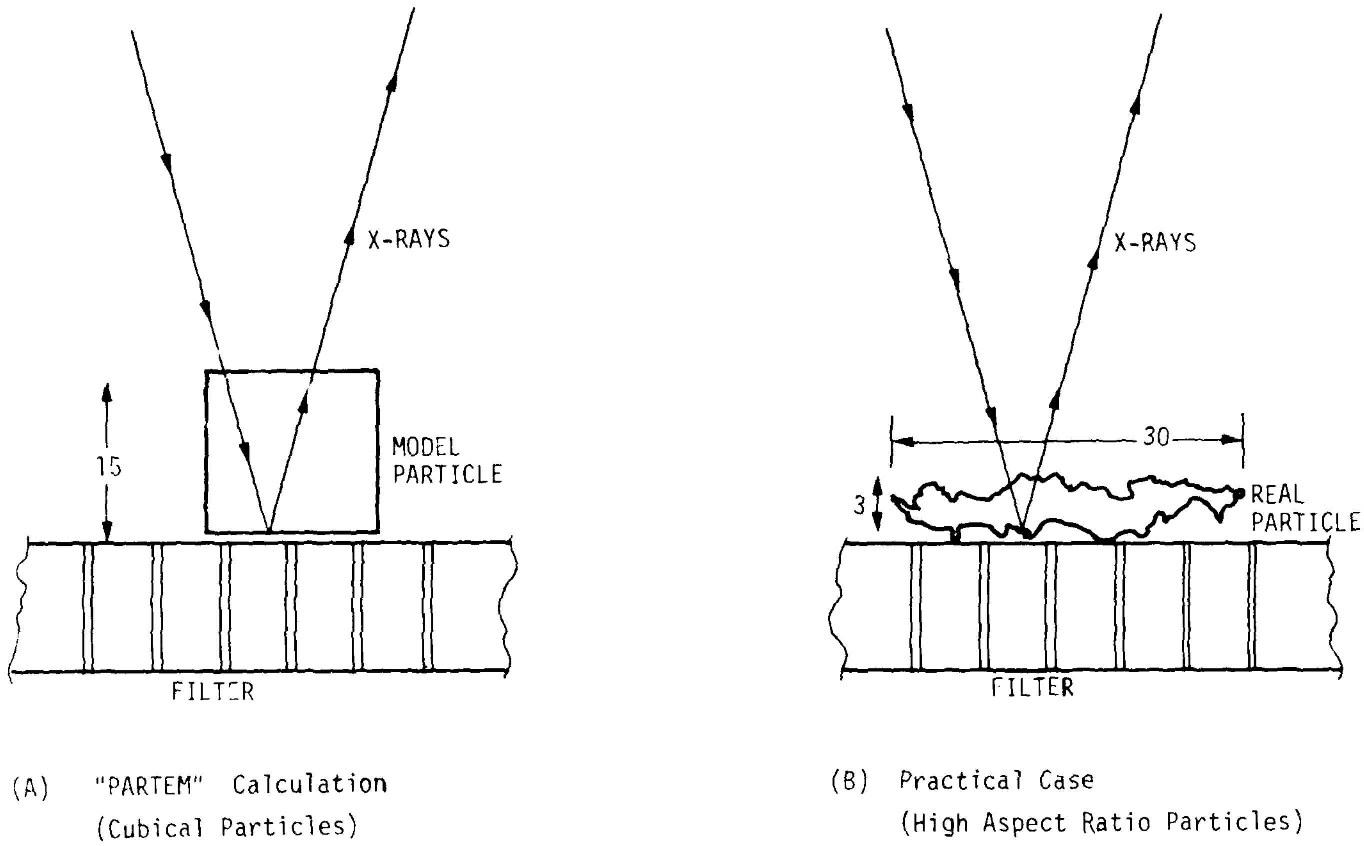


Figure 1-10
Plating Out of Filtered Particles
in Actual Case

Table 2-I COMPARISON OF DETECTORS

DETECTOR	TYPE	ABBREVIATION	RESOLUTION*	COMMENTS
Proportional Counter	Gas Filled	PC	1100 eV	Requires 1000 VDC Bias
Mercuric Iodide	Solid State	HgI_2	400 eV	R&D Devices Only
Silicon (Lithium drifted)	Solid State	Si(Li)	160 eV	Requires Cryogenic Operating Temperature

* For 5.9 keV x-rays (Fe-55 source)

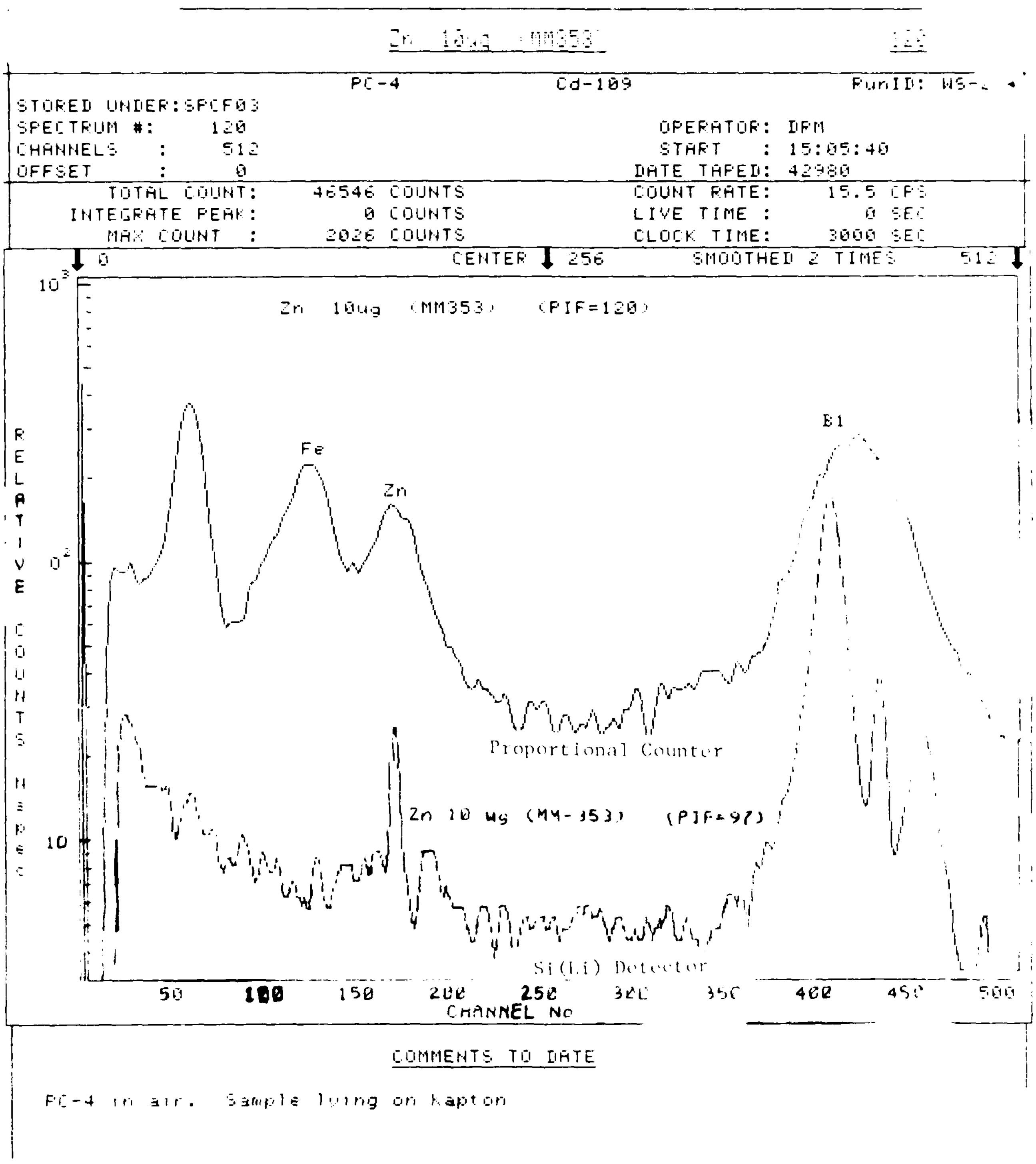
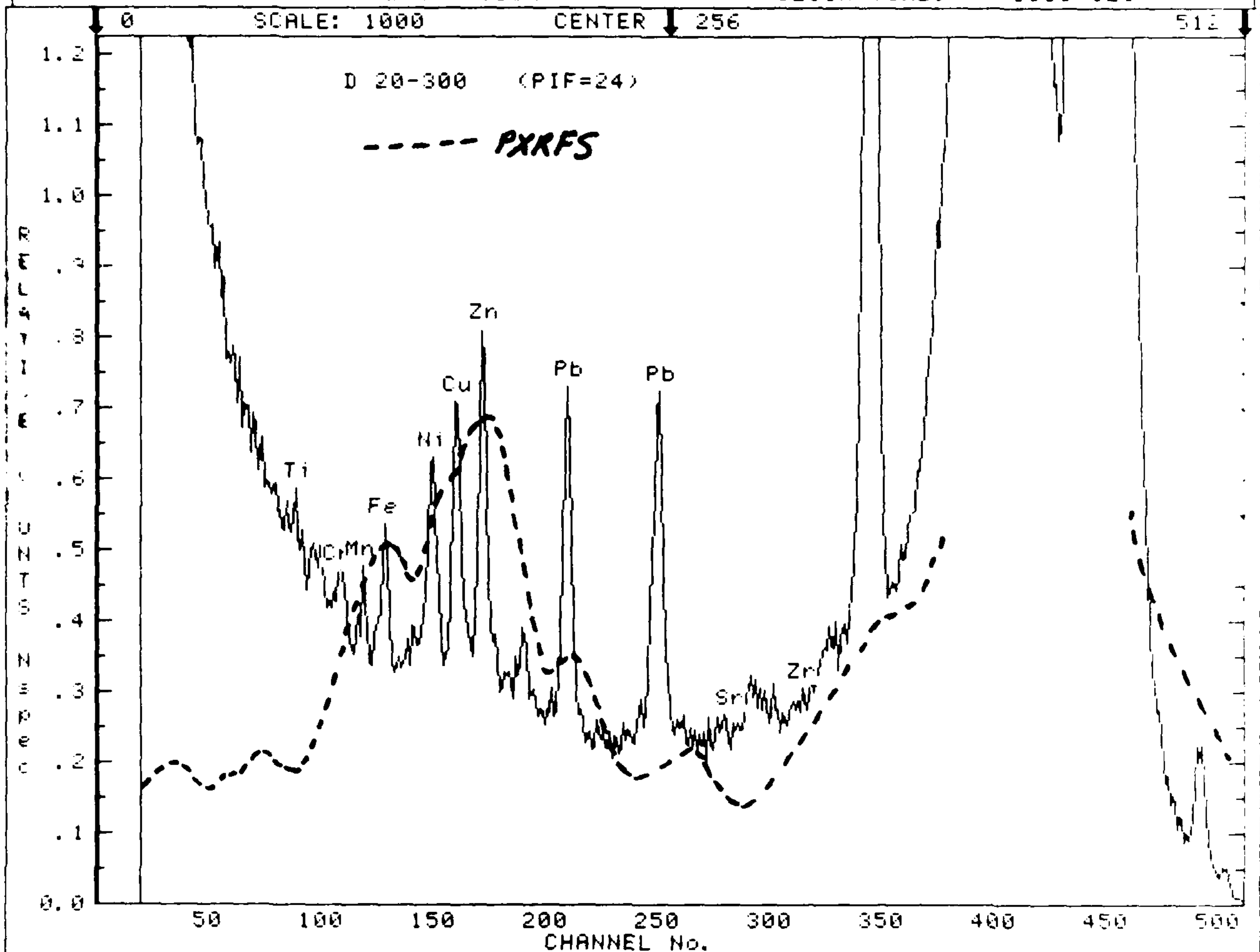


Figure 2-1
Comparison of Different Detectors

D 20-300

	Si(Li) Cd-109	RunID: MS-1?
STORED UNDER:SPCF07		
SPECTRUM #: 24		OPERATOR: DRM
CHANNELS : 512		START : 17:13:58
OFFSET : 0		DATE TAPED: 4280
TOTAL COUNT: 776733 COUNTS		COUNT RATE: 258.9 CPS
INTEGRATE PEAK: 0 COUNTS		LIVE TIME : 0 SEC
MAX COUNT : 28876 COUNTS		CLOCK TIME: 3000 SEC



COMMENTS TO DATE

In air. JOAP Oil sample. Batch
#R-2

Figure 2-2
Runs of Sample D20-300 Using
Si(Li) Detector and Proportional
Counter Detector from PXRFS

Silicon Detector

This detector is by itself very small (the size of a large transistor), but accessory electronics and mounting hardware are much larger. The major operating consideration is that the detector must be operated at low temperatures, about $125^{\circ}K$, in order that the thermal noise be sufficiently low to produce a satisfactory signal-to-noise ratio. In conventional technique, a liquid nitrogen dewar is hard-mounted to the detector assembly via a cold finger. Condensation is prevented by thermally isolating the detector and cold finger in a vacuum. X-rays reach the detector through a thin beryllium window sealed to the vacuum jacket.

Several different companies now manufacture Si(Li) detector systems for laboratory use. Normally, these laboratory units incorporate large dewars, and the detectors are such that they cannot be allowed to reach room temperature without the possibility of being damaged. During the course of this study, however, two companies have introduced miniature-dewar Si(Li) systems which are specified to be allowed to be cycled to room temperature. We have also received privileged information about a third company who will introduce a similar unit in about mid-1982. Thus, there now exists an ample source for small, high-resolution x-ray detectors which could be applied to oil wearmetal analysis. The only remaining drawbacks to such systems are the higher cost and the need to provide a small amount of liquid nitrogen (about 1 1/2 liter) prior to taking data. A set of typical specifications for this type of detector is given in Table 2-II. A photograph of one manufacturer's unit is in Figure 2-3.

Because of the recent availability of these portable units, and because of its superior performance, the Si(Li) detector must be considered a leading candidate for this application. In a series of investigations of oil samples, we have used a laboratory silicon detector extensively. Many examples of spectra are presented within this report.

Table 2-II SPECIFICATIONS FOR SILICON DETECTOR PORTABLE ASSEMBLY (TYPICAL)

Weight: 9.5 lbs. (empty)
12.0 lbs. (LN filled)

Dimensions: 16 inches long, 7 inches diameter

LN Capacity: 1.4 liters

Holding Time: 12 to 16 hours

LN Fill Time: Initial .5 hr. fill; 2 hr. cool down; 5 minute refill

Construction Material: Stainless Steel

Detector Size: 30 mm^2

Detector Resolution: 170 eV

Beryllium Window: 0.5 mil

Cost: $10 K

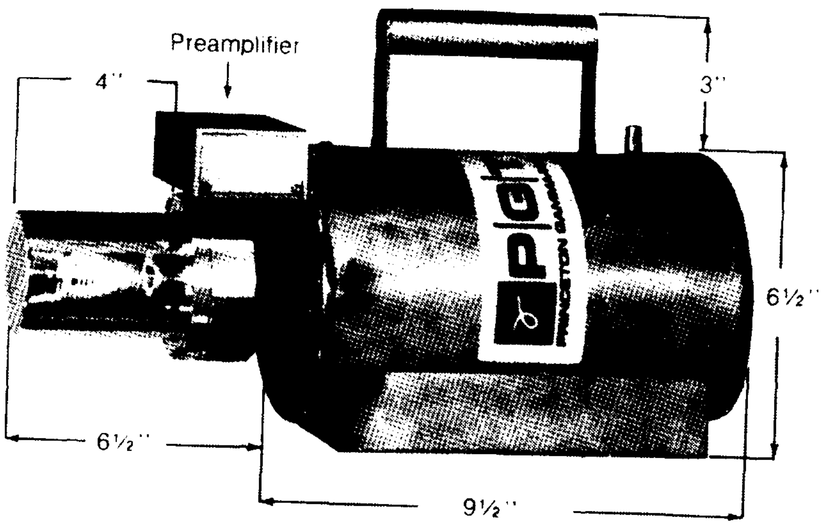


Figure 2-3
Princeton Gamma-Tech
Portable Si(Li) Detector

Three studies were done to test the precision of an x-ray fluorescence analysis using x-ray tube excitation, a Si(Li) detector, and filtered oil samples. In the first study, we constructed a sample series by mixing a weighed amount of iron particles (1 um diameter microspheres made from carbonyl iron) into a known volume of clean MIL-L-7808H engine oil and then making dilution standards from the starting mixture. From these standards, 3.5 ml aliquots were taken and filtered through 0.45 um Tyrann^{C} filters. An analysis of each filter is plotted in Figure 2-4, which establishes a calibration curve for this particular set-up and procedure. The resultant is seen to be quite linear, and sensitive at the lower end to a change as small as 2 ug Fe, equivalent to a concentration of 0.7 ppm Fe in oil. Operating conditions for these data were:

X-ray tube:	Au target, 30 kV, 0.5 mA
Time:	400 seconds
Detector:	Si(Li)

In the second study, we used small quantities of a bulk sample of used engine oil, designated JOAP-U1. For these samples, we filtered different size aliquots, ranging from 1 to 3.5 ml oil. The results of analysis for the elements Fe, Cu, Zn, and Cr were smooth and monotonic, but not linear, as seen in Figure 2-5. The nonlinearity may result from the amount of polymer degradation product, which could not be kept constant for this experiment since aliquots of various size were taken. Because of the linear results obtained with the clean oil (previous figure), we believe the bending over of the curves is sample rather than detector related.

In the third study, runs were made of five separately prepared samples of 3.5 ml each of JOAP-U3. The purpose of this test was to evaluate precision, i.e., repeatability, of the preparation method and analysis. No special precautions were taken and no monitoring of the gold-targeted x-ray tube output was included. The tube was powered off during sample change-out. Data were taken for 200 seconds for each sample. Spectra were analyzed for the three strongest peaks, which included iron, copper, and zinc. Results are recorded in Table 2-III. As would be expected, precision decreases with the level of element in the sample. Some additional improvement in precision can probably be attained by increasing the counting time or the x-ray tube output, and by standardization and control of the preparation procedure.

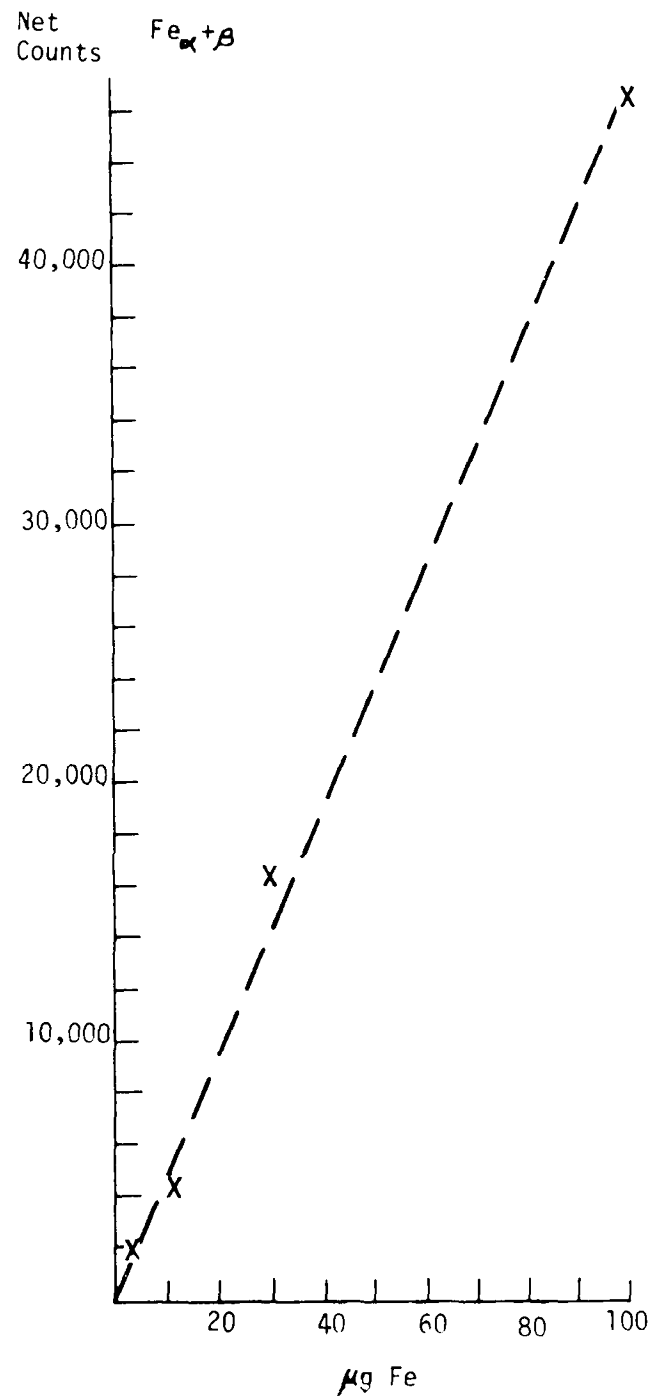


Figure 2-4

Iron Calibration Standards

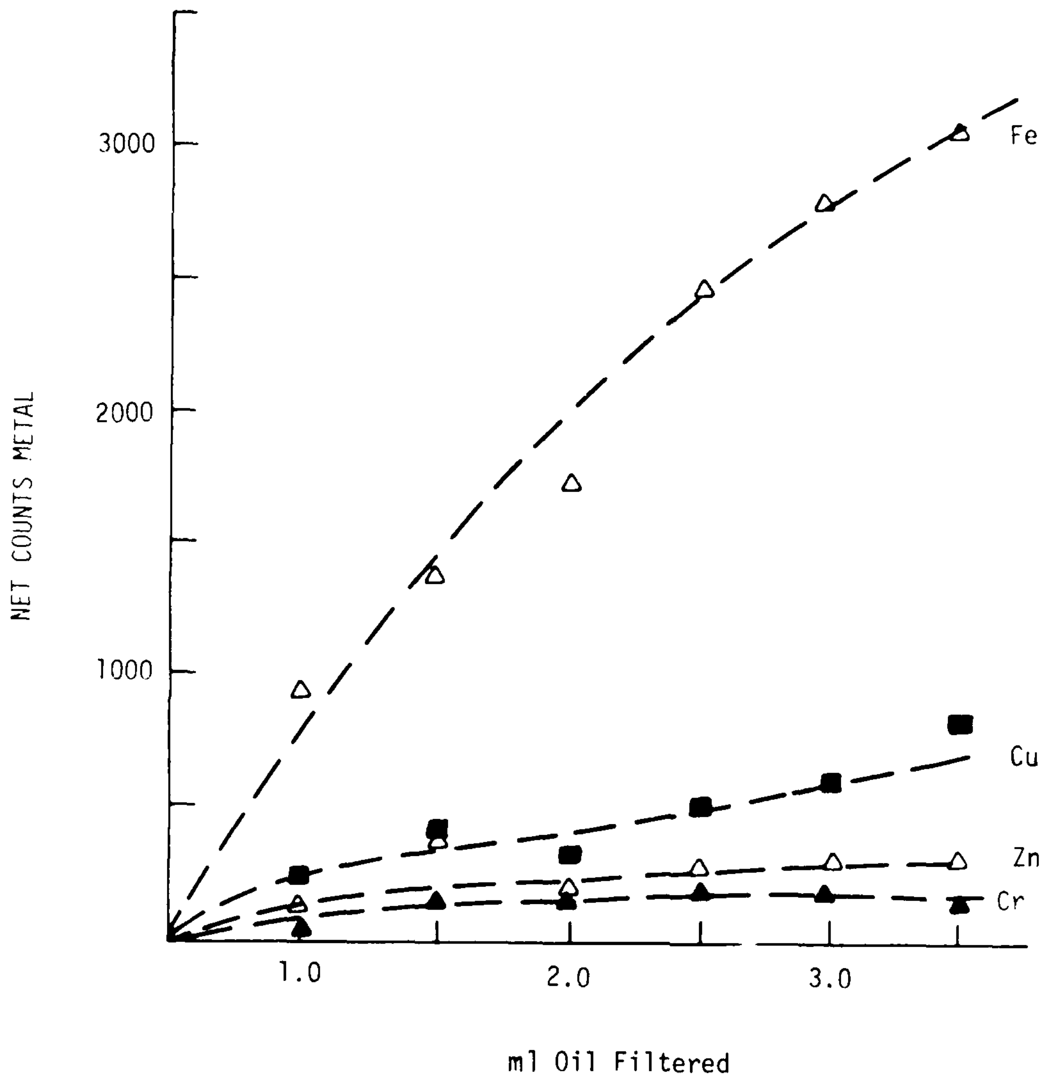


Figure 2-5
JOAP-U1, Varying Volumes

Table 2-III   Precision Test of Replicates

Elements	Mean Net Counts*	Relative Standard Deviation: Expected From Counting Statistics	Measured
Fe	19,000	0.7%	3.1%
Cu	1,500	2.6%	6.9%
Zn	590	4.1%	11.0%

* Total counts in peak, corrected for background

Mercuric Iodide Detector

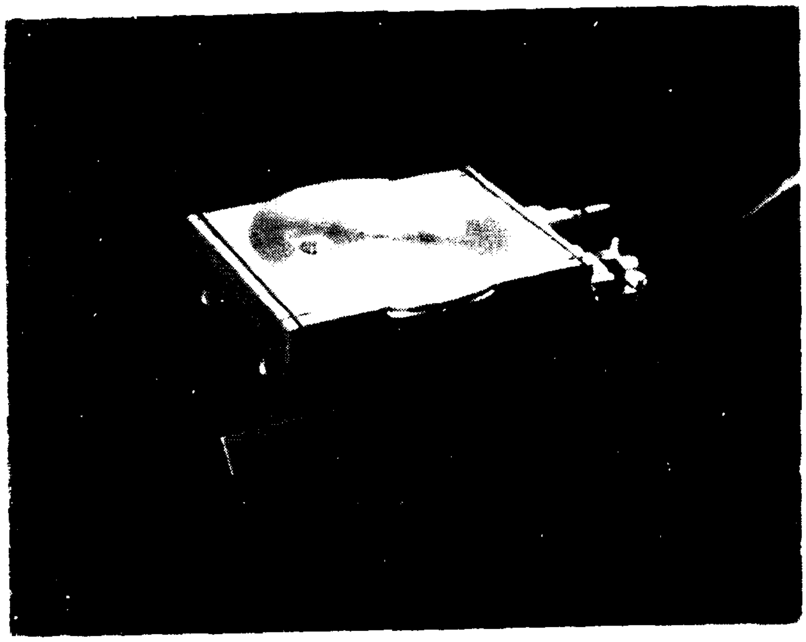
This type of detector is currently still under research and development, but is very promising because of its superior resolution over the proportional counter type of detector. Unlike the Si(Li) detector, it does not require cooling to cryogenic temperatures for operation, because of its much higher conduction band energy gap.

Although a commercial manufacturer at one time attempted to offer this device for sale, no deliveries have been made. At least two well-established manufacturers of silicon detectors are currently developing HgI_2 detectors in-house; neither has offered a product for sale. Several research projects are underway around the world, but the most successful results to date have come from the group of Dabrowski and co-workers at the University of Southern California's Institute for Physics and Imaging Science. We have purchased an HgI_2 detector system from this group and evaluated its application to the oil wearmetal analysis program.

Specifications for this detector are given in Table 2-IV, and a photograph of the detector mounted within its preamplifier unit may be seen in Figure 2-6. Several samples previously analyzed with the Si(Li) or PC detectors were analyzed with the HgI_2 detector under the same conditions. As can be seen in Figure 2-7, this HgI_2 detector produces a very sharp, clean line profile for a monoenergetic x-ray source such as Fe-55. One drawback, however, is the detector's very small active area, only one-tenth that of our laboratory silicon detector. Spectra of sample JOAP-10 taken with both the silicon and mercuric iodide detector are shown in Figure 2-8. The "raggedness" of the HgI_2 spectrum is mainly due to the lower counting rate (small active area). The muted nature of the Cr and Ar peaks may be a combination of low-channel background noise and poor efficiencies for x-rays of lower energies because of a relatively thick electrode coating on the front of the detector. The latter could be overcome by refining the coating procedure; the problem of low-channel noise may also be subject to reduction using guard-ring and other techniques.

Table 2-IV SPECIFICATIONS FOR MERCURIC IODIDE DETECTOR

Energy resolution for 5.9 keV	less than 450 eV (FWHM) HgI_2
Energy resolution for the pulser	less than 330 eV (FWHM) HgI_2
Sensitivity	0.49 mV/keV HgI_2
Active area of the detector	approximately 3 mm^2
Thickness of the "x-ray window" over the detector	approximately 30 um of Al
Output pulse polarity	positive
Detector bias voltage	-300 Volts
Power requirements:	
voltage	$\pm$ 10 V to $\pm$ 14V
current	32 mA
Dimensions (exclusive of connector and feet)	
inches approx.	4.2 x 1.6 x 3.3
cm	10.5 x 4.1 x 8.2



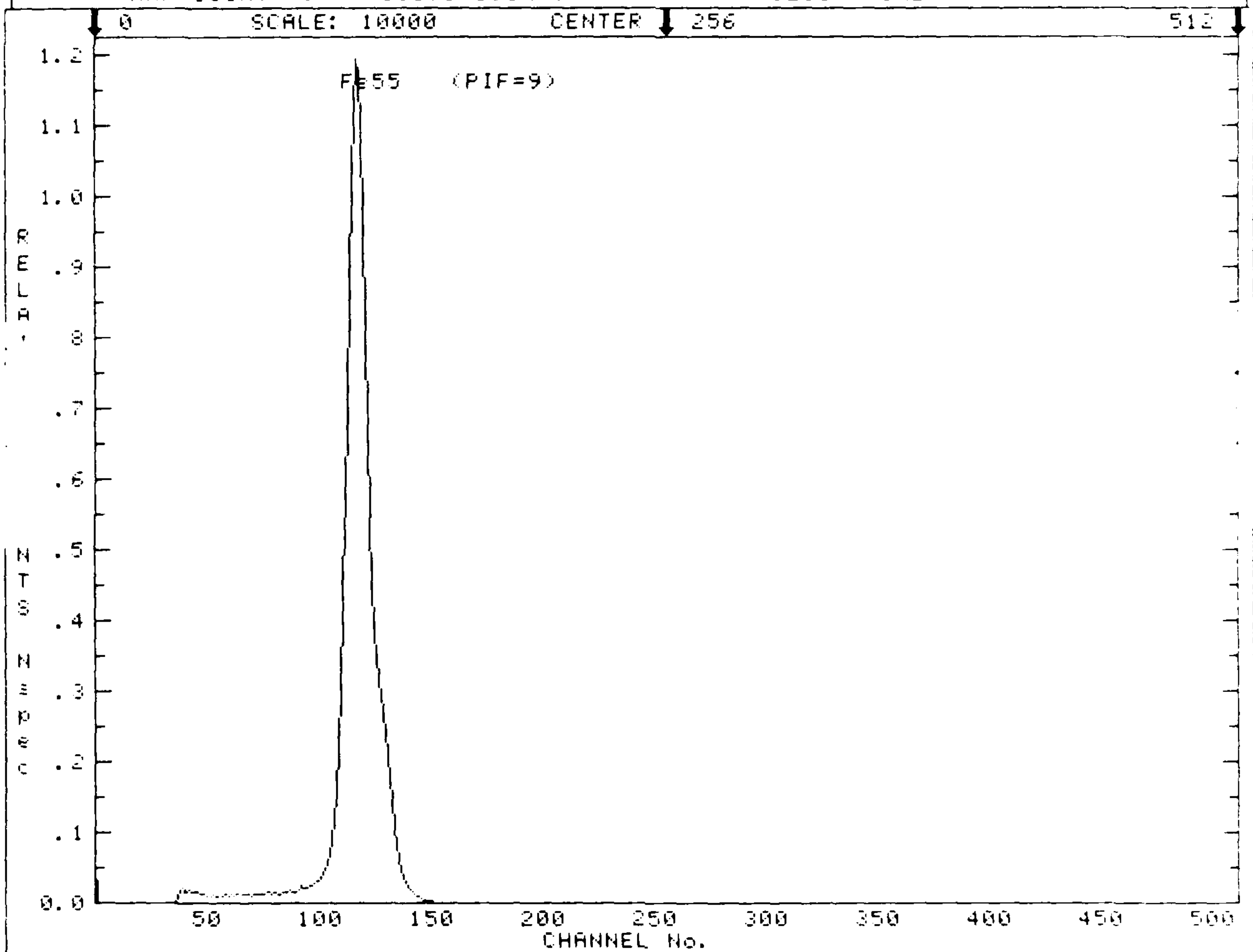
Fe55

Fe-55 RunID: HG-10-

STORED UNDER:SPCF10
SPECTRUM #: 9
CHANNELS : 512
OFFSET : 0

OPERATOR: OPAL CHEN
START : 12:58:14
DATE TAPED: 6980

TOTAL COUNT:	1000 COUNTS	COUNT RATE:	0.0 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	11691 COUNTS	CLOCK TIME:	626 SEC



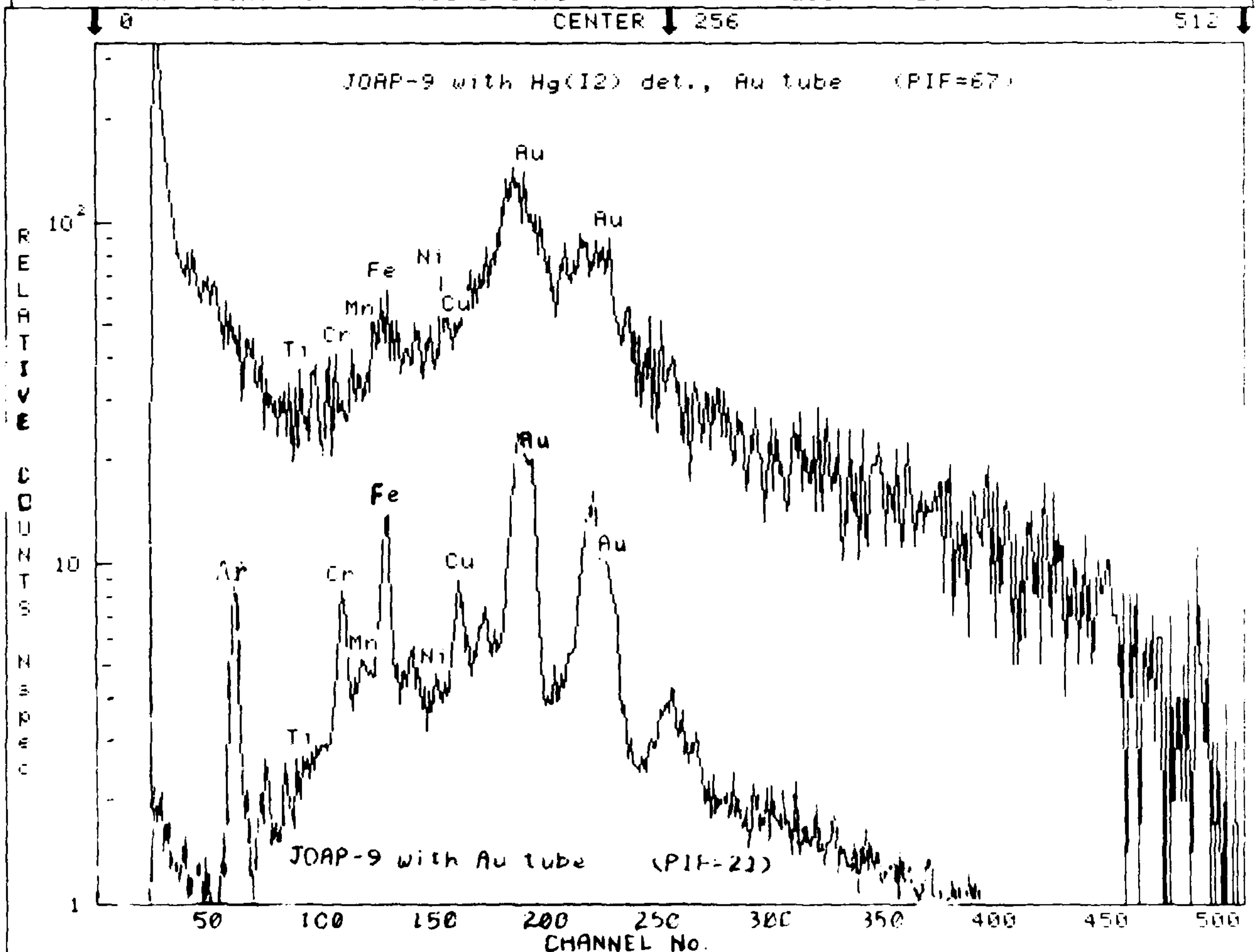
COMMENTS TO DATE

NO COMMENT

Figure 2-7
HgI_2 Spectrum of Fe55 Source

JOAP-9 with Hg(I2) det., Au tube 67

	HgI2	Cd-109	RunID: OW-4?
STORED UNDER:SPF08C			
SPECTRUM #: 67		OPERATOR:	bjc
CHANNELS : 512		START :	13:07:59
OFFSET : 0		DATE TAPED:	11581
TOTAL COUNT:	17487 COUNTS	COUNT RATE:	35.0 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	365 COUNTS	CLOCK TIME:	500 SEC



COMMENTS TO DATE

3.5 ml oil on Tyrann with Hg(I2) detector, Au x-ray tube. In air.

Figure 2-8
Comparison of Si(Li) and
HgI_2 Detectors

Studies of a number of JOAP samples and calibration standards gave good results for elements such as iron. For example, the calibration standards curve (ref. Figure 2-4) was just as linear and nearly as sensitive as for the silicon detector. The variable-aliquot curve was also good, but the scatter was greater due to the poorer counting statistics, and the two elements Cr and Zn could not be determined because of peak overlaps. Overall, the mercuric iodide detector gives good results for major elements, has better resolution but much smaller active area than the proportional counter detector.

3. Alternative Excitation Sources

Many different methods for stimulating x-ray emission are possible. Certain techniques, such as electron beam excitation, produce undesirable high backgrounds, and other methods, for example proton irradiation, require large complex laboratory equipment (e.g., particle accelerators). For portable equipment, there are two practical alternatives - radioisotopes and x-ray tubes.

Radioisotope Sources

Most radioactive isotopes can stimulate x-ray emission, but for greatest yield, lowest background, and for radiation safety reasons, the best are electron capture isotopes. These decay via removal of an electron from an inner shell into the nucleus, thereby creating a vacancy whose subsequent filling is attended by emission of a fluorescent x-ray. These x-rays may then be used to create vacancies, via the photoelectric effect, in the material being irradiated, resulting in x-ray fluorescence of the material. To stimulate fluorescence, the impinging x-ray must be of an energy higher than the binding energy of the electron in its shell - these critical energies are called the "absorption edges" in x-ray physics and are reported for priority wearmetal elements in Table 3-I.

Table 3-1
Key X-ray Energies (keV) for the Highest Priority Wearmetal Elements and Candidate Sources

Element	Absorption Edge	Principal Emissions Lines	Principal Emissions Energies
Ag	25.5	K alpha	22.16 keV
Ag	(3.35, 3.52)	L alpha	2.98
Ag	3.81	L beta	3.15
Ti	4.97	K alpha	4.50
Fe	7.11	K alpha	6.40
Cu	8.98	K alpha	8.04
Source			
Cd-109	N.A.	EC (Ag K)	22.16
Fe-55	N.A.	EC (Mn K)	5.90
Cr x-ray tube	5.99	K alpha	5.41
Au x-ray tube	11.92	L alpha	9.71
Au x-ray tube	(13.7-14.4)	L beta	11.44

The best detection sensitivity for a given element is usually achieved when the excitation energy is only ten or twenty percent above the absorption edge for the element. Only a few radionuclides decay via electron capture, however, and the practical choices for this application narrow to the isotopes iron-55 and cadmium-109. These isotopes have half-lives of 2.6 years and 1.25 years, respectively. Their emission energies are given in Table 3-I. Wearmetals including Cr, Fe, Cu, Zn, and others up to Mo in the periodic table are best excited by the Cd-109 emissions. Elements such as Mg, Al, Si, Ag, and Ti are best excited by Fe-55 x-rays. Figure 3-1 shows the relationships between various source and fluorescent x-ray energies. A number of experiments have been accomplished using these radioactive emitters. If it were not for the fact that their intensity is so low that analyses can take up to hours in data accumulation time, these sources would be ideal since their x-rays are virtually monenergetic. In addition, however, radioactive materials require licensing, periodic leak testing, and prior arrangements for interstate or international transportation.

X-Ray Tubes

The x-rays from an x-ray tube are actually comprised of two components, the fluorescent x-rays of the target material and a background radiation spread over all energies. This background is named bremsstrahlung radiation, and is generally undesirable since the lower energy components, when scattered, appear as a background in the detector spectrum. To minimize the bremsstrahlung and to maximize the monoenergetic characteristic radiation, the x-ray tube should be operated at a high voltage setting between two and three times greater than the absorption edge of the material in the tube target. This is not always practical since very high voltages entail large equipment and are difficult to generate.

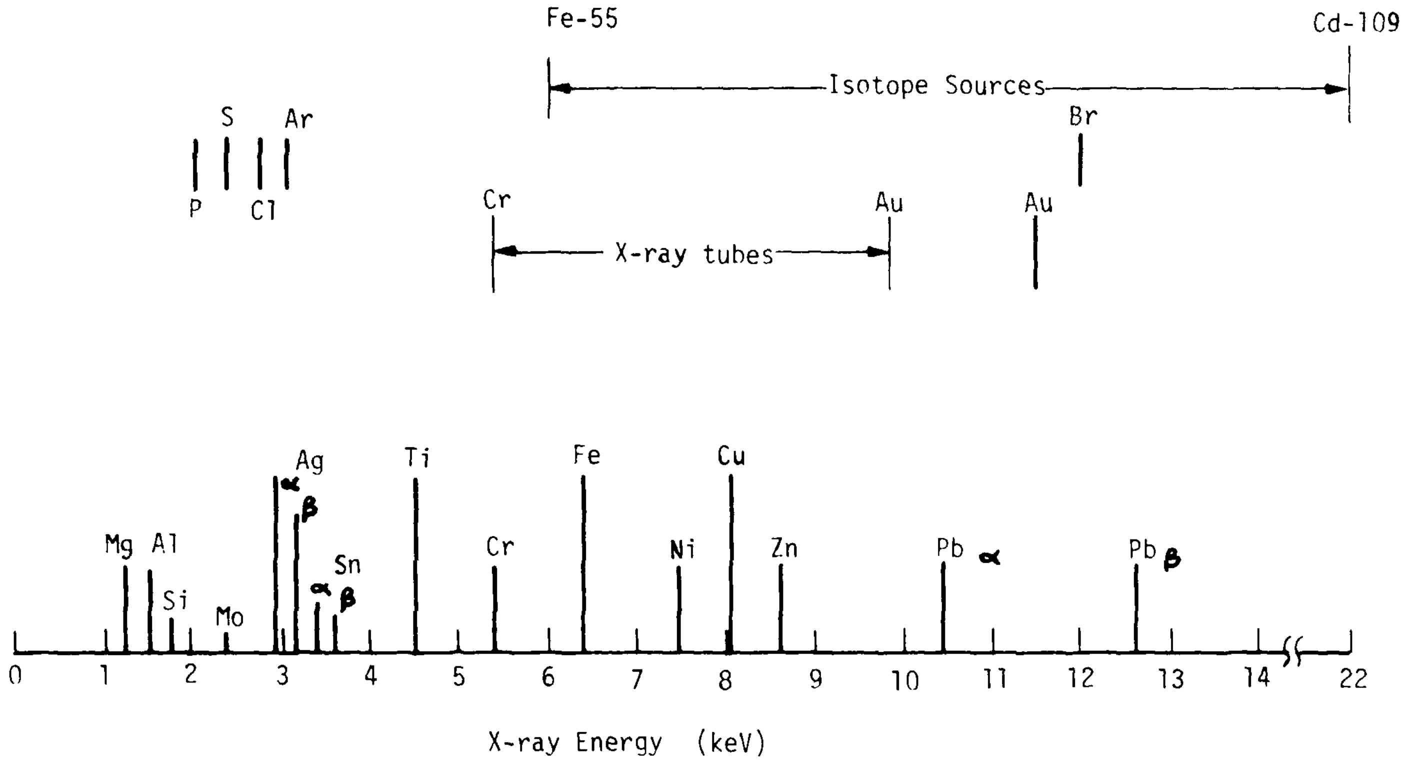


Figure 3-1
Relationship Between Source and Fluorescent X-Ray Energies

We have conducted a study of the optimum x-ray energies and target materials for oil wearmetal analysis. A copper-targeted tube produces a very strong copper line which is an excellent excitation for Fe, Mn, Cr, and Ti. However, the elements Ni, Cu, and Zn are obscured or not excited by the Cu line. A better source would be of a higher energy, such as the K lines from molybdenum or silver, both of which are satisfactory as x-ray tube targets. Unfortunately, the optimum power supply would be nearly 60 kilovolts, which is out of the question for a portable instrument.

A practical compromise is to use a gold (Au) target in the tube to generate L lines, whose energies are above the absorption edges of all the elements previously listed, including Zn. For more efficient excitation of elements with lower energy x-rays, such as Mg, Al, Si, Ag, and Ti, we would recommend a target producing lower initial energy. The most suitable material here is chromium.

Thus, for the most universal application, we would recommend two x-ray tubes, or, alternatively, a dual-targeted (switchable) tube. On the other hand, there may be applications where only certain elements need be detected and a single tube would suffice.

Many examples of various excitation sources are present within this report, including Fe-55 and Cd-109 isotope sources and copper- and gold-targeted x-ray tubes. Most spectra taken using x-ray tubes required less than 500 seconds data collection time in order to achieve reasonable statistics. Indeed, we observed many cases where the Fe peak from a filtered sample was evident in the spectrum after only 5 seconds of data taking.

Two additional studies were conducted with regard to excitation sources. The first was an attempt to produce a polarized beam of x-rays, which permits analysis of fluorescent x-rays from the sample with much reduced scattering background. The second study was related to the problem of detecting silver in oil samples.

Polarized X-Ray Sources

A collimated x-ray beam can be polarized by reflecting it at 45^0 incidence. If this beam is allowed to excite a sample, the amount of scattered radiation when observed from a direction perpendicular to the plane containing the incident and reflected beam paths is very small. Indeed, theoretically it is zero, although practical limitations prevent it from being entirely so. A new approach to this technique is to increase the efficiency of reflection by perhaps up to 4 orders of magnitude through use of a single crystal whose exposed Bragg plane diffracts the x-rays at $0 = 45^o$. To implement this approach, we have developed a computer program "XTAL1" for searching the (hkl) indices of candidate crystals for various x-ray excitations of interest. The latter are limited to x-ray tube lines (because of intensity considerations) and include copper, chromium, and gold-targeted tubes.

The computer results allow selection of those crystals most promising, taking into account the absorption effects for the incident x-ray. Optimum crystals and their cutting planes included magnesium (123) for the Au L-alpha x-ray; copper (012) for the Cr K line; and copper (113) for the Cu K line. In tests using a cut copper single crystal and Cu K-alpha x-rays, we had difficulty achieving high intensity in the polarized beam. Information recently obtained from experiments conducted at Lawrence Livermore Laboratory* indicate the improvement that can be expected is of the order of one to 1 1/2 orders of magnitude reduction in background. This would be useful, but not adequate, in improving the sensitivity for analysis of metals in bulk oil samples. The chief disadvantage of this approach is that the lowered intensity due to the tight collimation considerably increases the time required for analysis of trace elements.

*R. W. Ryon, J. D. Zahrt, P. Wobrauschek, H. Aiginger, UCRL-85836, 1981.

Silver Studies

One of the four or five key elements for engine wear-analysis is silver. In x-ray analysis of silver, the lines that can be excited include both the K and the L group of lines. The former are predominantly at 22.2 keV, and the L lines produce two main peaks at lower energies, 2.98 and 3.15 keV.

In our studies, we have examined the possibility of exciting either group of lines. Efforts to fluoresce at 22.2 keV were made using both an x-ray tube and a high-energy x-ray isotopic source, Am-241. In the case of the x-ray tube, it was found that excitation is not efficient unless extremely high voltage systems are used. The isotopic source does excite silver fairly well, but the increased Compton scattering due to the high energy involved (60 keV) tends to mask the silver line when the element is present at low concentrations.

Success has been achieved, however, using a low energy source to excite the silver L lines. In these tests, a 5.9 keV excitation and a vacuum path were used. Some spectra of interest are attached. Note that sample JOAP-15, Figure 3-2, shows even less silver (marked as Ag in the region of channels 210 to 230 on the curve) than in the subsequent spectrum for JOAP-4, Figure 3-3. This was puzzling to us since the former was reported to contain 1.9 ppm of Ag, while the latter was reported at only 0.4 ppm. This mystery was solved when a repeat analysis was performed by the SOAP laboratory at WPAFB (courtesy Howard Jones), and it was found that JOAP-15 indeed does <u>not</u> contain significant levels of silver.

An even stronger Ag peak than for JOAP-4 can be seen in the spectrum for JOAP-23, Figure 3-4. Here, the Ag doublet is quite pronounced, even though the reported level is only 0.7 ppm.

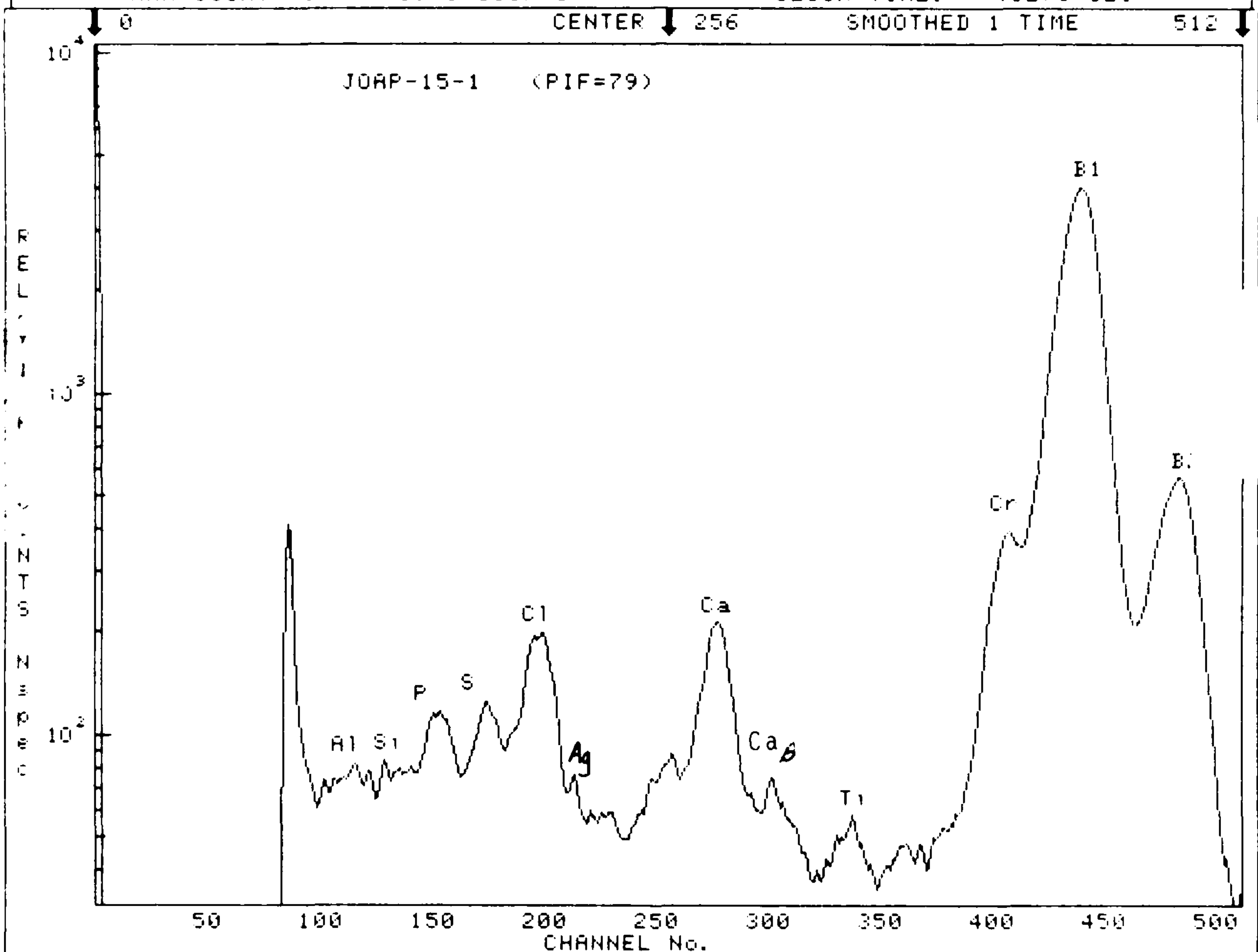
Si(Li) Fe-55 RunID: OW-268

STORED UNDER:SPF08B
SPECTRUM #: 79
CHANNELS : 512
OFFSET : 0

OPERATOR: BClark
START : 06:15:31
DATE TAPED: 41981

TOTAL COUNT: 125283 COUNTS
INTEGRATE PEAK: 0 COUNTS
MAX COUNT : 3978 COUNTS

COUNT RATE: 3.1 CPS
LIVE TIME : 0 SEC
CLOCK TIME: 40275 SEC



COMMENTS TO DATE

in Vac. on Nucl.

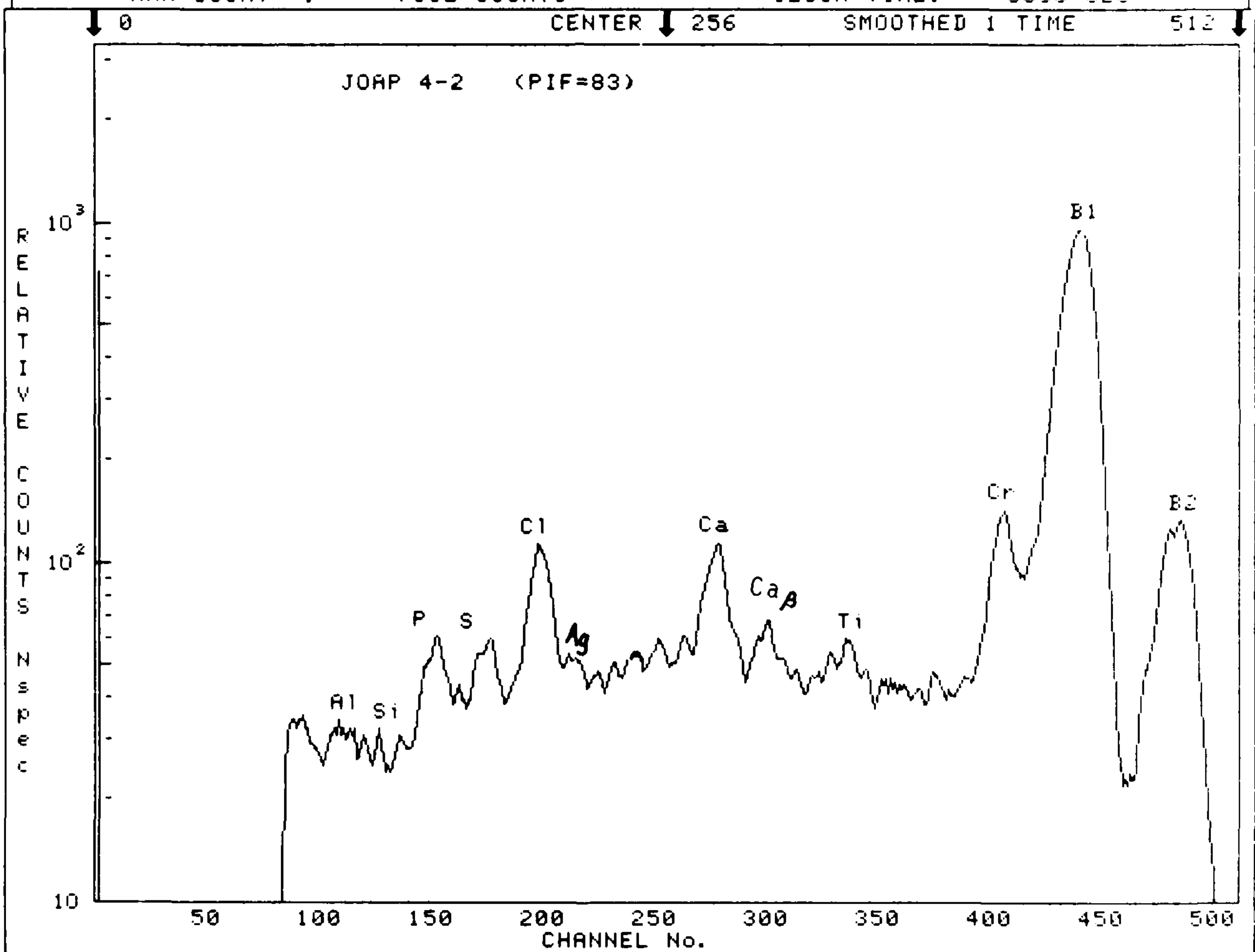
Figure 3-2
Spectrum of JOAP-15

JOAP 4-2

Si(Li) Fe-55 RunID: OW-272

STORED UNDER:SPF08B
SPECTRUM #: 83 OPERATOR: BClark
CHANNELS : 512 START : 14:11:29
OFFSET : 0 DATE TAPED: 42381

TOTAL COUNT:	44146 COUNTS	COUNT RATE:	6.4 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	7052 COUNTS	CLOCK TIME:	6858 SEC



COMMENTS TO DATE

" cycling. in Vac. 5 ml on Nuclepore.

Figure 3-3
Spectrum of JOAP-4

JOAP 23-1

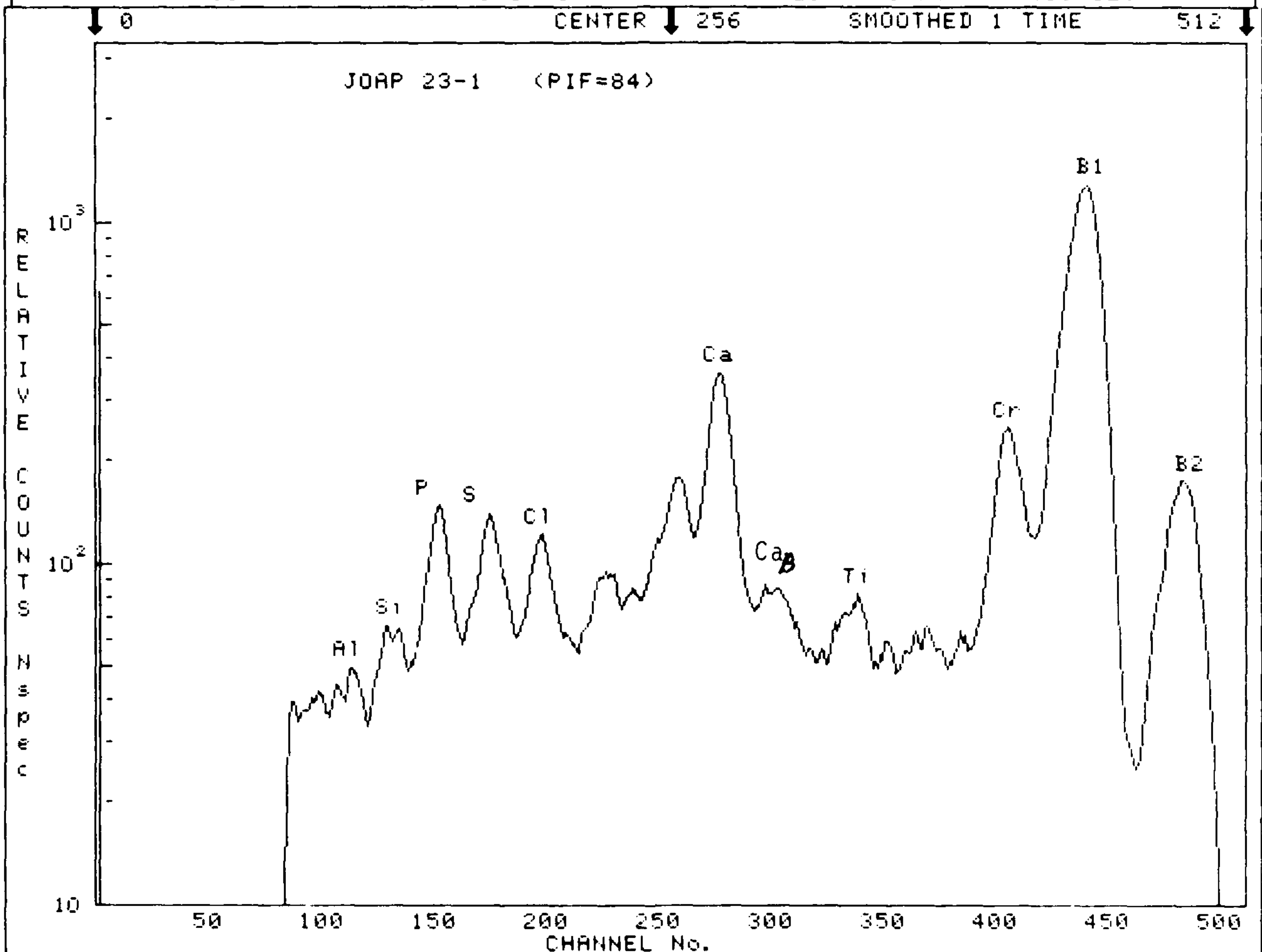
Si(Li) Fe-55 RunID: OW-273

STORED UNDER:SPF08B
SPECTRUM #: 84
CHANNELS : 512
OFFSET : 0

OPERATOR: BClark
START : 14:13:41
DATE TAPED: 42381

TOTAL COUNT: 55212 COUNTS
INTEGRATE PEAK: 0 COUNTS
MAX COUNT : 7052 COUNTS

COUNT RATE: 9.2 CPS
LIVE TIME : 0 SEC
CLOCK TIME: 6000 SEC



COMMENTS TO DATE

in Vac. No cycling of Si(Li) detector. 5 ml on Nuclepore.

Figure 3-4
Spectrum of JOAP-23

To accomplish further testing, three samples (F-50, F-58, and F-39) were provided to us by Becky Newman of WPAFB. Two of these were found to contain astonishingly high levels of lead and other elements; it was subsequently learned that these samples were from diesel engines rather than jet engines. The third sample, F-39, (Figure 3-5) produced an interesting spectrum which includes a very strong silver fluorescence line. To date, we have not received independent analytical data for these samples. Based upon extrapolations from the few samples we do have, our estimate of the silver content of F-39 would be 20 ppm. Analyses by K. Eisentraut place the silver content of this sample at 7 ppm. (Private communication from P. Centers, April, 1982).

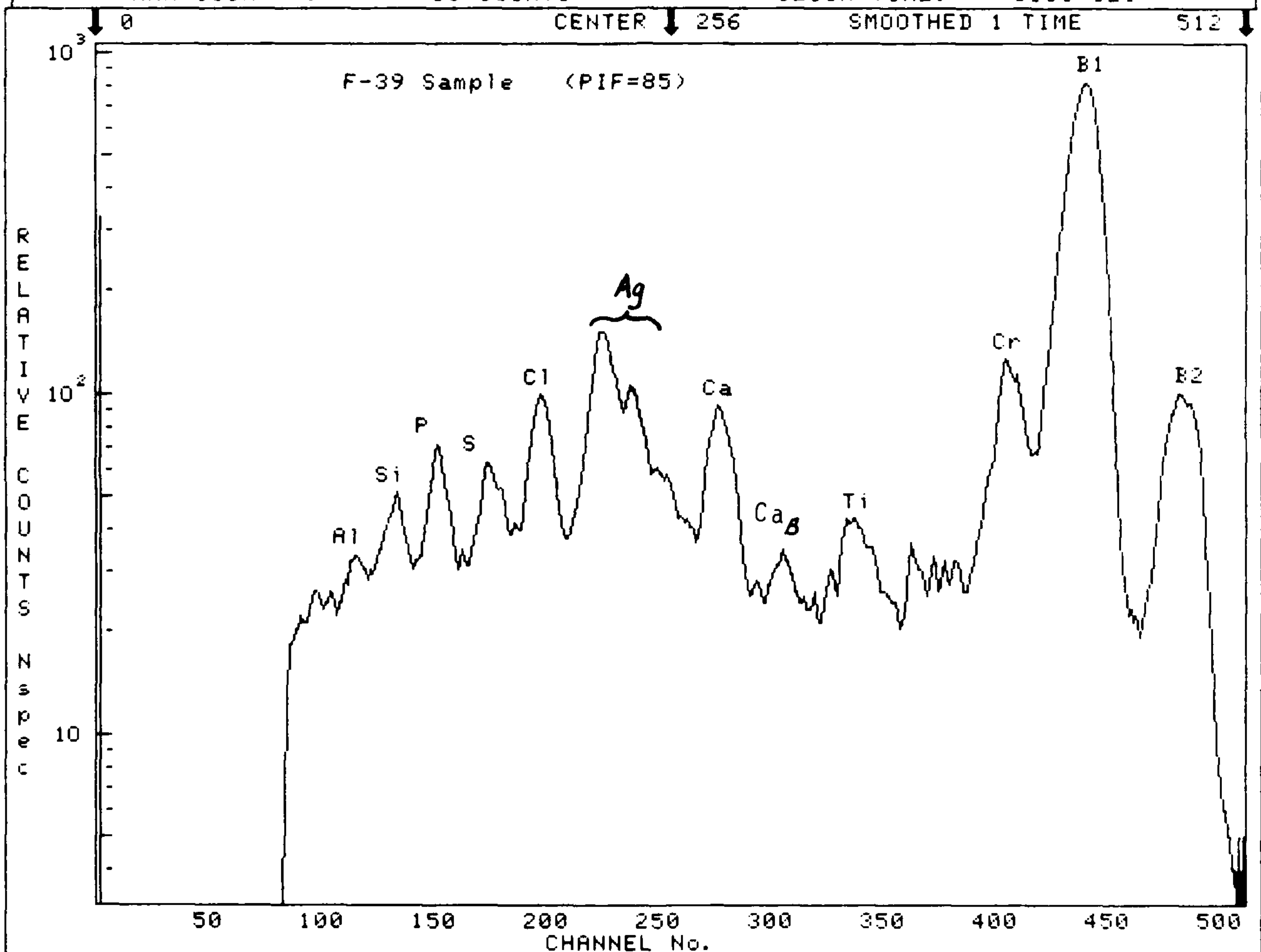
In summary, the feasibility of measuring silver wearmetal by x-ray fluorescence has been demonstrated. The implementation of this capability will require the use of an inert-gas path, or else special collimating optics to prevent interference from argon gas (present in air) K line fluorescence.

4. Instrument Trade-Off Studies

The instrumental factors of x-ray fluorescence technique which may be selected for this application are summarized in Table 4-I. The problem is fundamentally a three component one, with each component having from 3 to 8 alternatives. To some extent, alternatives from one component are affected by alternatives from another component. Without wide-ranging prior experience and some key studies using laboratory equipment and wearmetal samples, the trade-off study would become unmanageable. Fortunately, the problem components are sufficiently orthogonal (i.e., noninteractive) and the results of the theoretical analyses and experimental measurements have been sufficiently definitive, that judgements can be made to deduce a preferred approach.

F-39 Sample 85

	Si(Li)	Fe-55	RunID: OW-274
STORED UNDER:SPF08B			
SPECTRUM #: 85			OPERATOR: BClark
CHANNELS : 512			START : 07:23:49
OFFSET : 0			DATE TAPED: 42481
TOTAL COUNT:	31911 COUNTS	COUNT RATE:	10.1 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	781 COUNTS	CLOCK TIME:	3166 SEC



COMMENTS TO DATE

3 ml thru Nucl. in Vac. Special "Ag-containing" sample from Becky

Figure 3-5
Spectrum of F-39

Table 4-I TRADE-OFFS (Oil Wearmetal Analysis)

Source	Sample	Detector
Cd-109 Disk	Bulk Oil	PXRFS Hi
Fe-55 Ring	Thin layer	PXRFS Lo
X-ray tube	Filtered Particles	PC (OWAX optimized)
Direct (Cu, Au, Mo, Cr)		HRPC
Secondary Target		
Polarized		GSPC
		HgI_2
		Si(Li) (LN_2 cooled)
		Si, ion implanted

Excitation Source

Trade-off considerations for the x-ray source were as follows:

(1) The necessity for short analysis times (500 seconds or less), the low sensitivity for bulk analyses, and the difficulties in filtering large quantities of oil combine to rule out the use of radioisotope sources. An x-ray tube is the only practical alternative.

(2) Polarized x-rays require too long an analysis time because of their relatively weak intensity.

(3) A secondary target may be useful, especially for silver analysis, but is not required for analysis of most elements provided a high resolution detector is used.

(4) The optimum target for analysis of the group of elements Ti, Cr, Fe, Ni, Cu, and Zn is gold. The optimum target for Ag is chromium.

Sample

A thin layer of bulk oil sample can be more accurately analyzed than a thick sample because less scattered radiation is present in the spectrum. An optimum thickness is 0.1 to 1 mm for most elements. The level of improvement in sensitivity is between a factor of 2 and 20. However, additional complexities in sample holding, and cleaning of the window, as well as the necessity of having a very thin window, argue against this approach.

By far the most powerful method of enhancing sensitivity is to preconcentrate the wear debris. This could be done by centrifuging, by magnetic attraction (including ferrography), or by filtration. We prefer the last option because of the ease of automation and the relatively short time needed to process the sample. In the sections which follow, detailed discussions address how various problems have been overcome with engine oil filtration. The benefits are very great, about a factor of 100, in sensitivity. Although bulk analyses are probably quite feasible for "dirty" engines, the very low wear debris content of the oil in high performance jet engines is beyond the sensitivity of portable x-ray fluorescence equipment without the filter concentration technique.

Detector

Proportional counters, even if optimized specifically for the oil wear-metal application, will have some difficulty in achieving accurate analysis for less abundant constituents. The typical high iron content will tend to mask out the Ni concentration, and will affect the accuracy to which Cr, Cu, and Zn can be determined. There will be strong interferences between Cu and Zn, as well as between Ti and Cr. With a highly stable system and computer spectrum deconvolution, it may be possible to analyze these interferences.

The High Resolution Proportional Counter (HRPC) and the Gas Scintillation Proportional Counter (GSPC) offer enhanced resolution. But neither are available commercially; the resolution improvement of the HRPC is very modest; the GSPC is bulky, needs very high voltages, and can operate only with pure xenon, which exacerbates the scattered spectrum interference problem.

The mercuric iodide detector is for the time being eliminated from consideration because of not being a reliable, commercially-available product. From what was learned in the experimental studies during the course of this work, it is now known what specifications need be applied to such detectors. The possibility of future availability is high, but the time period is too uncertain for current planning.

The ion implanted silicon detector for x-ray spectrocopy is a recent commercial development, but its resolution still cannot compete with even the proportional counter detector.

Overall, then, the most promising alternative is the portable Si(Li) detector with an integral, miniature dewar for liquid nitrogen cooling. One may hope, of course, that the on-going extensive research in many different laboratories may soon result in a breakthrough in room temperature high resolution x-ray spectroscopy.

5. Sample Handling Methods

Initially, we investigated sample handling and treatment techniques with the idea of adapting the Portable X-Ray Fluorescence Spectrometer (PXRFS) to use with aircraft engine oil samples. However, as our investigations progressed, the concept of a two-box oil analysis system evolved and came to include a method for preparing oil samples for analysis. Of prime importance in sample preparation techniques were a) ease of use; b) strength of x-ray transmission; c) minimization of extraneous fluorescence and scattered background noise; d) chemical and physical compatibility with diester-base lubricants; and e) the economy of each method. Another goal in the investigation was an improvement in sensitivity over that of the PXRFS.

We considered several methods to achieve these goals. The first was the use of a thin sample, which would reduce the amount of backscattered signal. The thin sample method was rejected, however, since the difficulty in obtaining a reproducible thin sample wasn't justified by the improvement in sensitivity. The second method investigated was the optimization of the sample holder. This method involves a preferred angle-of-reflectance substrate, and requires both that the sample be very thin and that the carrier oil be removed by oxygen-plasma ashing. Since the sample preparation required is so extensive and since the perfection of the alignment and polishing fineness of the substrate surface need constant maintenance, the method didn't seem feasible if many samples were to be analyzed in a short period of time. Finally, we decided to develop a method for preconcentrating the wearmetal particles. This method promised to be the most appropriate for use in an automated system, as it only requires that the oil be vacuum filtered through a membrane filter. Since no elaborate treatment is needed, it is also practical for rapid analysis of many samples. Furthermore, the apparatus to analyze preconcentrated samples could include the option of analyzing bulk samples.

Adopting the filtration method required that the procedure be semi-automatic. The operator would be busy inputting data concerning the sample as well as handling the general logistics of processing a large number of samples each day. Also, standardized techniques are necessary for analytical accuracy of the highest caliber. We have designed and tested a system which simplifies the procedure from the operator's viewpoint.

Design of the Quantitative Filtration Assembly (QFA) was constrained by the guiding principle that it be simple to use and "operator proof." This means that with only a few minutes of instruction and practice, the operator should be able to do filtrations successfully and routinely. It also means that individual component faults or non-standard procedures attempted by the operator should not induce jamming or other catastrophic failure of the entire unit. In detail, the requirements included such things as 1) need to meter out a 3 ml aliquot from the sample introduced, 2) a guide to limit overfill (20 ml of sample), 3) ability to dispose of spill-over in the event a sample did not filter properly, 4) prevention of sample addition before the re-assembly of filter and metering block is complete, 5) detection of completion of the filtration step, 6) a swirling rinse step, 7) moat reservoir cleanup, and 8) ultimate disposal of used liquid samples from the holding tank.

The design adopted is shown schematically (not to scale) in Figures 5-1 and 5-2. Functionally, operation consists of pouring an amount of liquid to be filtered through an inlet funnel into a metering cylinder which is clamped over a filter; filtration is achieved by a combination of gravity and suction applied beneath the filter.

As can be seen in Figure 5-1, the inlet funnel is provided with an inlet cover, whose purpose is three-fold: 1) during the rinse cycle, solvent is pumped via the rinse inlet through a narrow tube (#18 hypodermic needle) up against the cover to produce a dispersion and swirling action, 2) to prevent splash-out during rinse, and 3) to prevent, via mechanical interlock, any introduction of sample at the wrong time. Note that the inlet funnel is not mechanically connected at its lower end (B) to the metering block. Clearance is provided so that the block can be raised during filter insertion; after lowering, the bottom end of the inlet funnel still nests within the block interior so that no danger of spillage exists when liquid is poured in.

Figure 5-1

QFA - Concept Schematic for Central Unit

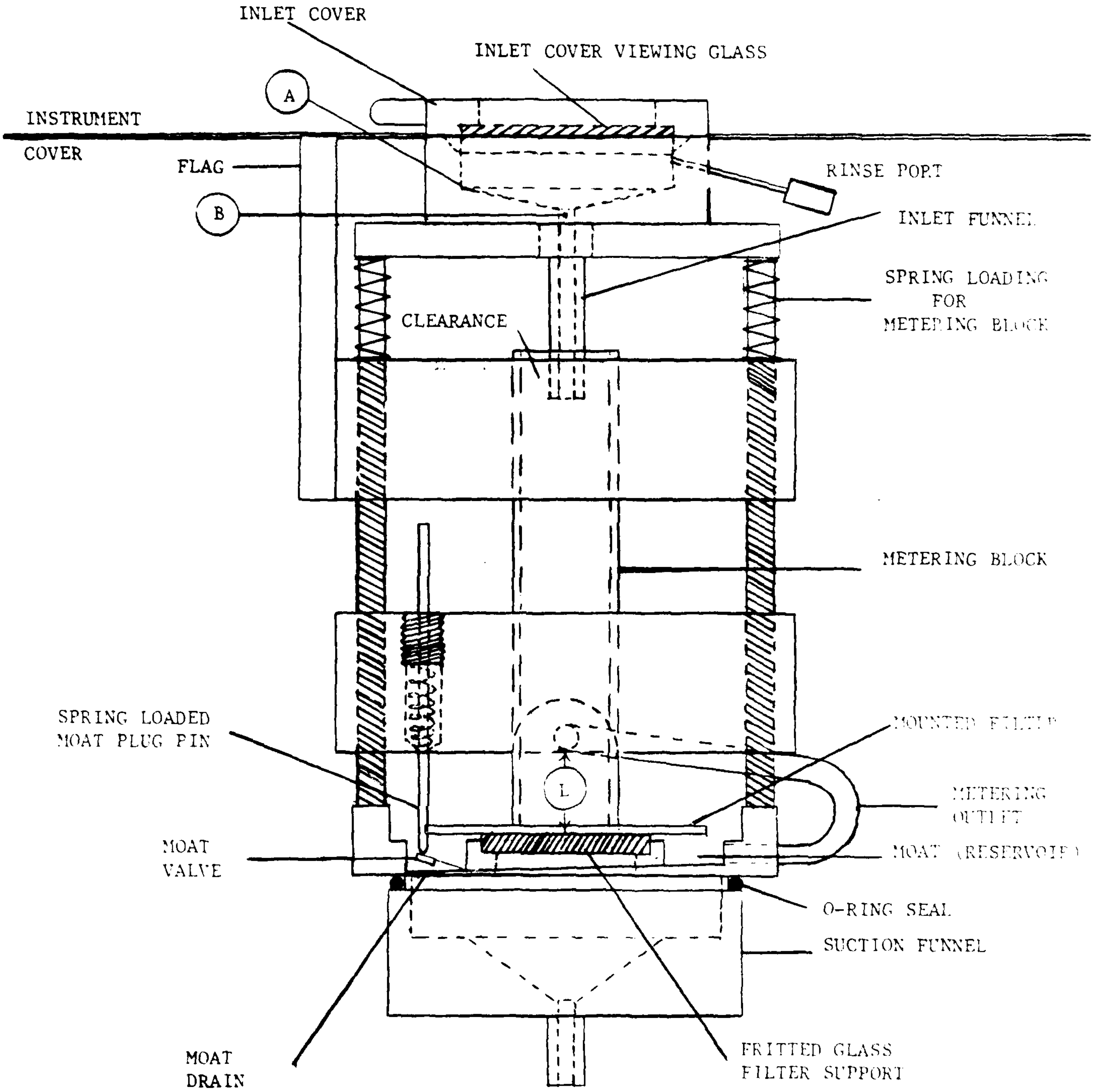
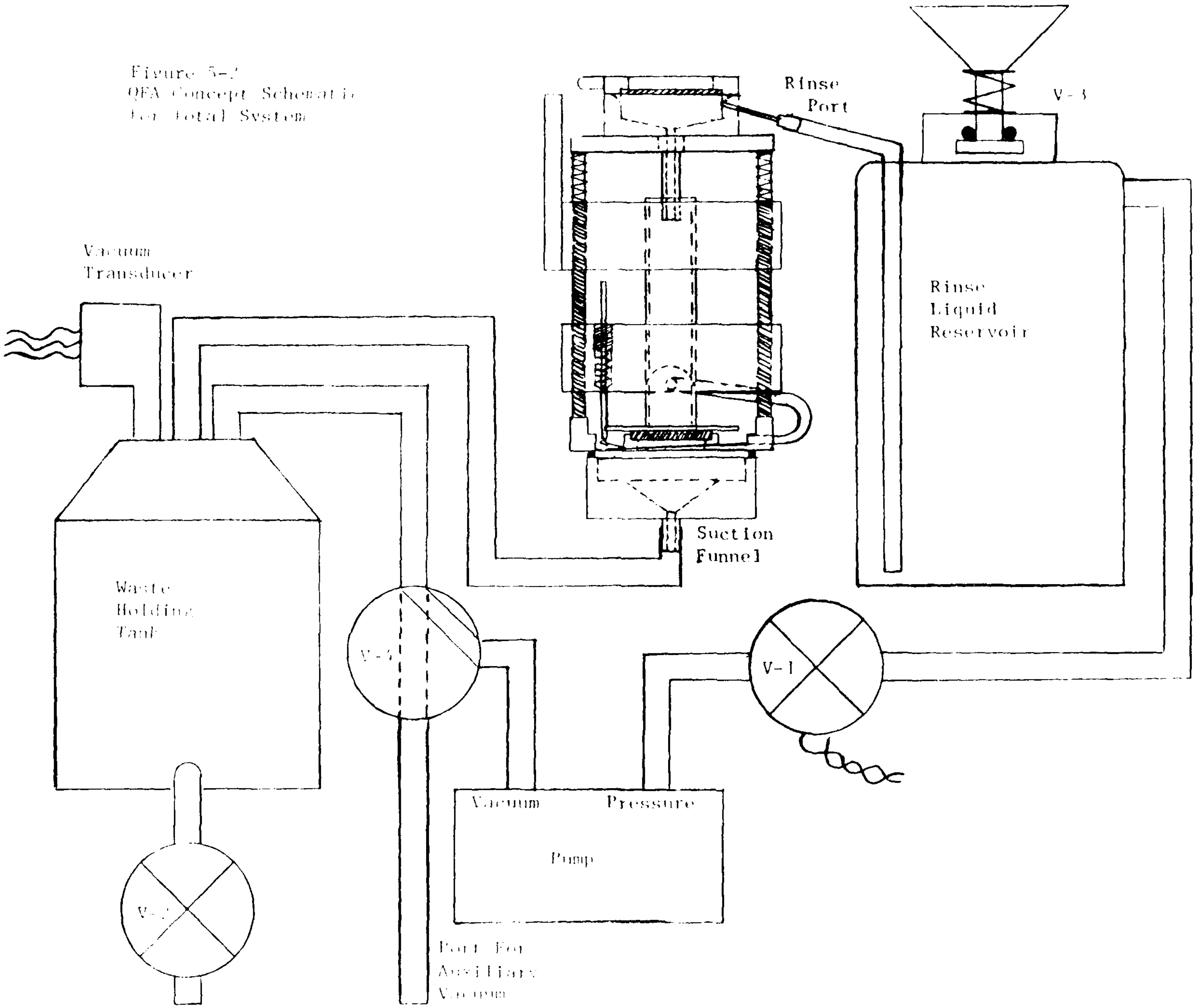


Figure 5-2
QFA Concept Schematic
for Total System



Metering the sample, i.e. taking a fixed 3 milliliter aliquot, is done by simply discarding the overflow through the metering outlet (situated at a height (L) above the base of the metering cavity) into the moat. Accurate and reproducible metering occurs provided that the filter is sufficiently impermeable that negligible filtration occurs in a time period of one second or so and is easily accomplished in most cases as long as no vacuum is applied, provided that the operator has supplied an adequate amount of sample. Attainment of the latter is aided by two additional design features: 1) a mark is inscribed at an appropriate level (A) in the inlet funnel, and 2) the length and bore of the funnel tube (B) are adjusted to slow delivery of the liquid to the block. With suitable adjustments of (A) and (B) for the viscosity of the type of liquid being filtered, it is possible to get quite good results. Furthermore, the system is self-compensating: if a person pours fast, he tends to fill somewhat above level (A) before stopping; if he pours slowly, the fill can be made precisely to the level (A), but by then a certain portion of liquid will already have passed through (B). For instance, repetitive experiments have shown that for our application of aircraft engine oil, the variance in the amount of sample delivered is less than 1 ml, ranging from 4.5 to 5.4 ml, depending upon pouring rate. This generates delivery of the minimum amount while at the same time assuring that excessive amounts of samples are not consumed.

Filters are mounted inside frames for ease of handling. We have used commercially available 35mm film holders as mounts. The filters are inserted into a slider shown mounted in the QFA in Figure 5-3, which is inserted to the distance necessary to position the filter above a filter support (a screen, fritted glass, or other). The metering block is then lowered by actuating a camshaft via the front-panel knob. Dual springs seal the block against the filter. At the same time, a moat plug pin, Figure 5-1, engages a moat valve which seals off a bypass moat drain to the suction funnel. At this point, all suction is applied through the filter support and filter, thereby forcing filtration. When filtration is complete, the block is raised with the vacuum pump still on. This opens the moat valve, allowing the original liquid which passed out the metering outlet to be drained. Drainage of the moat could also be necessary in the event that the filter had become plugged, with the filtration incomplete, if the block-to-filter seal were imperfect, or if the operator had somehow managed to introduce new sample without the block being lowered. Once the moat clean-up cycle is completed, the vacuum pump is shut off and the filter may be safely advanced.

Up to this point, the narrative has described the "manual" mode of operation. It should be noted, however, that we have also provided for motor drive of the slider assembly, as shown by the rack gear on the slider and the DC motor mounted to a pinion drive (see Figure 5-3). This motor is electrically interlocked via microswitch to prevent operation unless the metering block is in the up, "clean" position. It is also possible, in principle, to place the camshaft under motor drive control. Automatic position monitoring of both the slider and block can be via mechanically operated switches or by strategically placed phototransducers. An additional positioning function is served by the moat plug pin, which must pass through a clearance hole in the slider. Since this pin is spring loaded in the downward direction, a sharp click can be heard and felt when the slider is in the correct position; this registers the filter precisely. In the fully advanced position, for filter analysis, the slider is simply stopped by a back-stop.

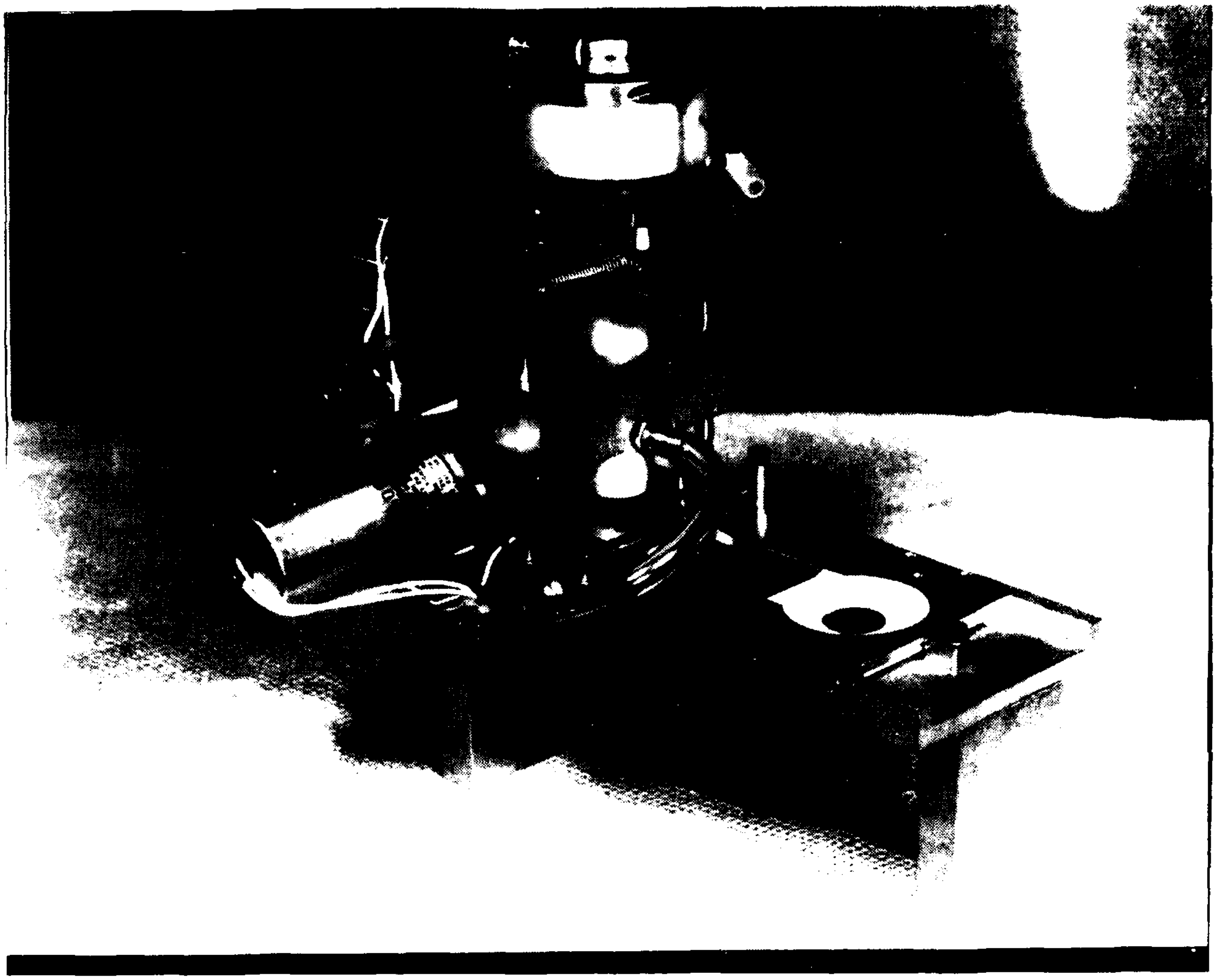


Figure 5-3
Quantitative Filtration Apparatus

The connection scheme between the central unit described above and the rest of the system is shown schematically in Figure 5-2. The pump is a dual function vacuum and pressure unit. The waste holding tank draws off the filtrate. Monitoring the degree of vacuum achieved with the vacuum transducer provides a method of automatically determining when the filtration is complete since the degree of vacuum suddenly becomes much less when the final amount of liquid penetrates the filter, leaving a relatively clear path to the atmosphere. Periodic draining of the waste holding tank is made possible by opening valve V-2, located on the front panel. A mechanical "Y" valve normally connects the pump to the tank, but in the event of pump failure, an external pump or a hand-operated vacuum pumping device may be connected to the "AUX VAC" port.

6. Sample Treatment

Having decided on the best approach to sample handling, it remained to perfect a technique for treating each sample. Used aircraft engine oil contains a sludge-like organic polymer which makes it difficult to filter through a 0.4 micrometer (um) membrane filter. It was desirable, therefore, to find a solvent which would allow easier, more rapid filtration. Using a 0.4 um Nuclepore filter, we discovered that the use of a ketone, such as acetone or methylethyl ketone (MEK) or of xylene, either as the pure product or as technical grade naptha, greatly improved the filtration time. Table 6-I provides a list of the solvents tested. We also discovered, however, that the improvement depended upon how the solvent was added; unless it was added in a way that stimulated mixing, it remained as a layer on top of the oil. Several methods of mixing were tested, including addition of solvent at the bottom of the sample chamber, adding oil and solvent together, and bubbling air through the oil/solvent mixture. All of these methods improved filtration time, but unfortunately it was difficult to conceive of a way to incorporate a provision for mixing into the design of the filtration mechanism. For this reason, we attempted to find a different means of filtering the oil.

Table 6-I Candidate Filtration Boosters

Effective	Ineffective
Acetone	Freons TF, TMC
MEK	1, 1, 1, TCE
Xylene	EtOH, MetOH, 1POH
	Chloroform
	Toluene
	Butanol
	MIBK
	Paint Thinner
	Ethyl Acetate
	Heptane
	Powdered and Liquid Detergents
	Pentane
	Amyl Acetate
	PE Glycol
	Turpentine
	Tetrachloroethylene
	Butyraldehyde

We originally chose Nuclepore filters for the procedure because their thinness greatly reduces the amount of backscattered radiation and because they appeared to be compatible with both acetone or MEK and xylene. However, upon comparison with other filters listed in Tables 6-II and 6-III, they gave the slowest rate of filtration of any filter tested. This seems to be a result both of the discrete pore size and of possible incompatibility with the oils tested. The filters which gave the best filtration rate were Purolator Puropore's Tyrann-ME. These filters are anisotropic and give, in effect, prefiltration which removes the polymeric sludge without losing any of the particulate wearmetals. Although they are not compatible with acetone, Tyrann filters are resistant to xylene, and the greatly improved filtration rate eliminates the need for mixing the oil and solvent during filtration.

The choice of xylene as a filtration booster meant that other materials used in the system needed to be chosen carefully. Viton tubing proved to be suitable for use in the connecting lines and vacuum pump fittings. Choosing a material for the waste and solvent containers presented a more difficult problem. Polyethylene is resistant to xylene for short term use, but swelling of the plastic could become a major problem over an extended time period. Other solutions to the problem include the use of fluorocarbon, glass, or metal containers, but these must be tested. Other materials tested for compatibility with solvents are listed in Table 6-IV.

To give ease of handling, the filters are mounted in 35mm slide mounts and are then simply inserted into a filter holder which fits into the filtration mechanism. The mechanism has been designed to suction filter each sample or if required, analyze bulk oil samples. In its final form, this method of sample handling and treatment will give accurate, reproducible results while reducing operator handling and at a cost of under $.80 per sample for materials.

TABLE 6-II COMPARISON OF TESTED FILTERS

FILTER	PORE SIZE, μM	THICKNESS, MG/CM^2	AVG TIME, MIN 3.5 ML OIL	NET FE	NET BKS	COMPATIBLE SOLVENTS	MANUFACTURER	MANUFACTURER'S COMMENTS	COST PER EACH
Nuclepore Polycarbonate,	1.0	1.13	1.25	490	1264	Acetone, Naphtha	Nuclepore Corp.	-Precise pore size cutoff -Chemical stability -Smooth, flat surface -Retains little liquid -Strong, flexible	$ .54
Capillary Pore	0.4	0.968	>60	421	1022				$ .43
Tyrann-ME	0.8	3.52	1 (estimated)	627	4636	Naptha	Purolatur Puropore	-Integral polymeric membrane -Anisotropic (graduated pore size) -50% better flow rate, greater throughout -Flexible, resistant to breakage	$ .45
Anisotropic Cellulosic	0.45	4.34	1.3	908	5728				$ .38
Nylon-66	0.45	4.16	3	837	8677	Acetone, Naphtha	Rainin	-Lower priced than PTFE -Sturdy -Chemically resistant to solvents	$ .50

TABLE 6-III OTHER FILTERS

FILTER	MANUFACTURER	AVAILABLE PORE SIZES	THICKNESS MG/CM^2	COST PER EACH	COMMENTS
Zetapor	AMF Cuno Div. Distributor: W.M. Murphy & Co. Engineered Industrial Products 5785 N. Sheridan Arvada, CO 80002 423-8370 ATTN: Paul Murphy	0.2 um 0.45 um	-	$ .35	- Nylon-66 - Compatable with Acetone - Short term compatability with Xylene - Adsorptive charge improves recovery
Silver Membrane	Selas Flotronics Div. 1957 Pioneer Road Huntingdon Valley, PA 19006	0.2 - 5.0 um	30.5	$ 5.00	- Compatable with Acetone and Xylene - Absolute particle size retention - No pore size degradation
Nylasorb	Ghia 7070 Commerce Circle Pleasanton, CA 94566 (800) 227-1245	1.0 um	-	$2.20	- Nylon - Sturdy, flexible - Compatable with Acetone, Xylene
Metricel-GA	Gelman Sciences, Inc. Ann Arbor, MI 48106 (313) 665-0651	0.2 um - 5 um	3.24	$ .43	- Cellulosic - Compatable with Xylene only
MF-Millipore Type HA	Millipore Corp. Order Service Dept. Bedford, MA 01730 (800) 225-1380	0.45 um	5.21	$ .29	- Cellulosic - Compatable with Xylene only

Table 6-IV

Materials Compatibilities with Solvents

MATERIAL	ACETONE	NAPHTHA (xylene)
Tubing:		
Tygon	softens, dissolves	softens, swells
Teflon (PTFE)	OK*	OK
Viton (flurocarbon rubber)	dissolves	OK
Polyethylene	OK	limited exposure OK
Polyproplylene	OK	softens, swells
Bottles:		
Polyethylene	OK	softens slightly
Polypropylene	OK	softens, swells
Adhesives:		
Duco Cement	dissolves	weakens
Tra-con #2129 Epoxy	weakens	OK
Elastomers:		
Neoprene	OK	swells
Red Sponge Rubber	OK	swells
Bulk Plastics:		
Lucite	dissolves	dissolves
Nylon	OK	OK

* OK denotes that the material does not react (physically or chemically) with the indicated solvent.

7. Methods of Data Storage, Retrieval, and Presentation

In choosing an appropriate data analysis system for the OWAX, we looked for a unit with the capacity to compile and present the answers to these questions:

a. What is the identity of this sample? i.e. which aircraft did the sample come from, what are the date and time?

b. Which metals, in what quantities, does the sample contain?

c. What maintenance or repair does the aircraft need?

In addition, the unit needed to be portable and compact, relatively inexpensive, and capable of providing electronic prompts to operate the analyzer unit. We chose the Hewlett-Packard 85 (HP85) professional computer.

The HP85, pictured with the OWAX analysis unit in Figure 7-1, is a compact, portable computer with 32K byte memory, BASIC language capability, and built-in lighted display. The unit is completely self-contained, with a thermal printer and magnetic tape mass storage included in one case. It is "suit case" portable and has an available carrying case. Specifications for the HP85 may be found in Table 7-I.

The software needed to operate the OWAX is stored on a compact magnetic tape cartridge. Because the HP85 uses the BASIC language, the software is user-oriented, requiring no special training for the operator. The software also enables the computer to control the analysis box hardware through an RS-232 interface.

The HP85 performs analyses by reading information from the OWAX microprocessor into an array. It converts the array into a spectrum, calculates the areas under the peaks, and converts these values to units of parts per million (ppm) metal. It will then print out all or part of the calculated results, according to the operator's desire.

Picture 7-1
HPS[illegible] (Right) and [illegible]MAS Analysis [illegible]

Table (7-I)
Hewlett-Packard 85 Desktop Computer
Specifications

Total Read/Write Memory
    Standard: 16K bytes
    Optional: 32K byte

Tape Cartidge
    Access: File by name
    Typical capacity: 200K bytes
    Search speed: 152 cm/s
    Read/Write Speed: 25.4 cm/s
    Rewind time: 29 s

Display
    Size (diagonal): 12.7 cm (5 inches)
    Capacity: 32 characters x 16 lines
    Graphics: 256 x 192 - dot plotting area

Thermal Printer
    Line width: 32 characters
    Graphics: Dot for-dot reproduction of CRT image

Interfaces available
    HP-IB IEEE 488-1978
    Bit serial RS-232C
    BCD Binary Coded Decimal
    General purpose 16-bit parallel

Size and Weight
    Height 15.9 cm
    Width 41.9 cm
    Depth 45.2 cm
    Weight 9.06 kg

Cost
    $3250 base

During an analysis run, the computer gives instructions to the operator as to when to add oil, raise and lower the meter block, and advance the filter holder. It also asks the operator for a sample identification code, which allows it to keep an updated file on each aircraft. By comparing a new sample from a given aircraft with previous samples from the same aircraft, the computer responds to changes in oil wearmetal levels and provides notice of needed service.

Figures 7-2 and 7-3 illustrate the interaction of the operator and computer. The operator is asked to input the type of aircraft and engine, along with the appropriate serial numbers. The computer establishes a data base and after a spectrum has been taken, outputs the information shown in Figure 7-3. The output includes a brief history of the engine, actual concentrations of each metal, and advised action. Should the concentration of a metal rise dramatically, as the level of titanium has in the simulated run, the computer outputs an alert.

Figure 7-4 summarizes the software which is part of the data handling system. The software includes programs which catalog given engine types and serial numbers, along with engine histories. In addition are the main programs which control data-taking and analysis.

The HP85 provides an optimum data handling system which will track sample, equipment identification, and wearmetal data, as well as assisting the operator in the associated decision-making process.

```
            Planes
 N    -Model-       -S/N-        -Tec-
 1   B8-324123A   CH-53A/D     BARA
 2   JA27-2223    CH-53A/D     ASAP
 3   JNTX1234     RH-5555      AHAB
 4   A13872       TH1LTGB      ASAK
Which Plane?

       Engines for A13872
 N   -Model-     -S/N-
 1   TH1L        157842
 2   TH1L        166623
 3   TH3L        80722543
 4   TH3LC       88890333
Which engine?
```

Figure 7-2
Operator Interaction with HP85,
Input

```
Run #   17        Date: 5-14-82
Lab: MMC Sim      Oper: Johnson
Equip model: JA27-2223
  Equip S/N: H-53A/D
  Equip TEC: ASAP

  Eng model: TH11
    Eng S/N: 80722543

Smpl    Date    -Hrs Since-
Num     Anal    Ovhl OilChg Reason

0170 2-23-82    527    56   Routine
0190 3-2-82     564    92   Lab Req
0200 5-7-82     593    23   Routine
0210 5-14-82    593    23   Lab Req


 ----PPM Readings----    Advice
  Fe Ag Cr  Cu  Ti Ni Cmptr   Lab

  27  0  1   78  0  4 NOR/SP   B
  25  0  0   80  0  4 NOR/SP   A
  55  0  2  160  1  8 Normal   C
  62  0  3  189 25  9 ALERT*   Z

 ------------------------------
| Smpl    TRENDS (ppm/10 hrs)  |
| I.D.  Fe   Ag   Cr   Cu   Ti   Ni |
|                              |
| 0190  -1    0   -0    1    0    0 |
| 0200  10    0    1   28    0    1 |
| 0210   4    0    1   15   13    1 |
 ------------------------------
```

Figure 7-3
HP85 Output

DATA MANAGEMENT

MAIN PROGRAMS SPECIAL PROGRAMS	PROGRAMS (40 KBYTES)
10 RUNS IN DETAIL 300 RUNS SUMMARY	RUNHIS 915 KBYTES)
200 PLANE-ENGINES (S/N'S, LOOK-UP ID'S)	PLNDB 95 KBYTES)
30 ENG. TYPES (7 TRIPS, 11 ELE'S)	CRITDB (5 KBYTES)
11 ELE'S X 2 SIZES LAST 10 ANALYSES DATE, RUN NO., HRS SINCE, ADVISORY'S	ENGHIS (100-180 KBYTES)

Figure 7-4
HP85 Data Management

MARTIN MARIETTA

8. System Optimization Study

Our primary goal in designing the OWAX was to produce a portable instrument which would be rugged, fast and simple to operate, and reasonably low in cost. In addition, we sought to maximize sensitivity, accuracy, and precision while maintaining the multi-element capability of the x-ray fluorescence method. Figure 8-1 and 8-2 list the criteria and goals toward which we worked.

Initial tests using the PXRFS to analyze engine oil samples showed that the x-ray fluorescence method was a promising one but that it would require some adaptations for aircraft oil wearmetals. We found that bulk analysis was difficult from the standpoint of particle-size independence, as the larger particles tend to settle out of the oil, out of the range of the x-ray beam. Also, the wearmetal concentrations in most high performance oils approaches the lower limit of detection for the x-ray method. Filtering the oil provides a means of improving particle size independence and, because it preconcentrates the wearmetal particles, it also improves precision and accuracy.

For dirty oils which have very high (50 ppm) wearmetal concentration, bulk analysis is still suitable. This is especially true since the older oils contain a large amount of organic polymer which makes them difficult to pre-filter. We intend to modify the metering apparatus for use with bulk oil samples. When modified, the apparatus would include a mechanism to trigger automatic suction removal of excess oil to give a sample of uniform thickness. Figure 8-3 is a sketch of the meter block modification for bulk analysis. The mount which holds the sample cup would be designed to bring the vacuum line into position when the operator inserts the mounted cup. The oil delivery tube and rinse system would also be redesigned in adapting the instrument for bulk oil analysis.

CRITERIA

PORTABILITY ("SUITCASE")

COST

SENSITIVITY/ACCURACY/PRECISION

MULTI-ELEMENT CAPABILITY

SPEED OF ANALYSIS

MINIMUM MAINTENANCE

MINIMUM CONSUMMABLES

SAFE

PRINTOUT

DATA RETRIEVAL AND EVALUATION

PARTICLE-SIZE INDEPENDENT

RUGGEDNESS

Figure 8-1
Criteria for OWAX Design

MARTIN MARIETTA

DESIRED GOALS

WEIGHT:	Less than 50 pounds
SPEED:	150 samples per 8 hours (3 min. per sample)
COST:	Under 35K per unit
POWER:	Accept 120 or 230 VAC at 50, 60, and 400 Hz
ELEMENTS:	Fe, Ti, Ag, Cu, Cr, Ni, Mo, Si, Al, Mg, (Pb, Sn, K, Ca, Mn)

Figure 8-2
Desired Goals for
Instrument Design

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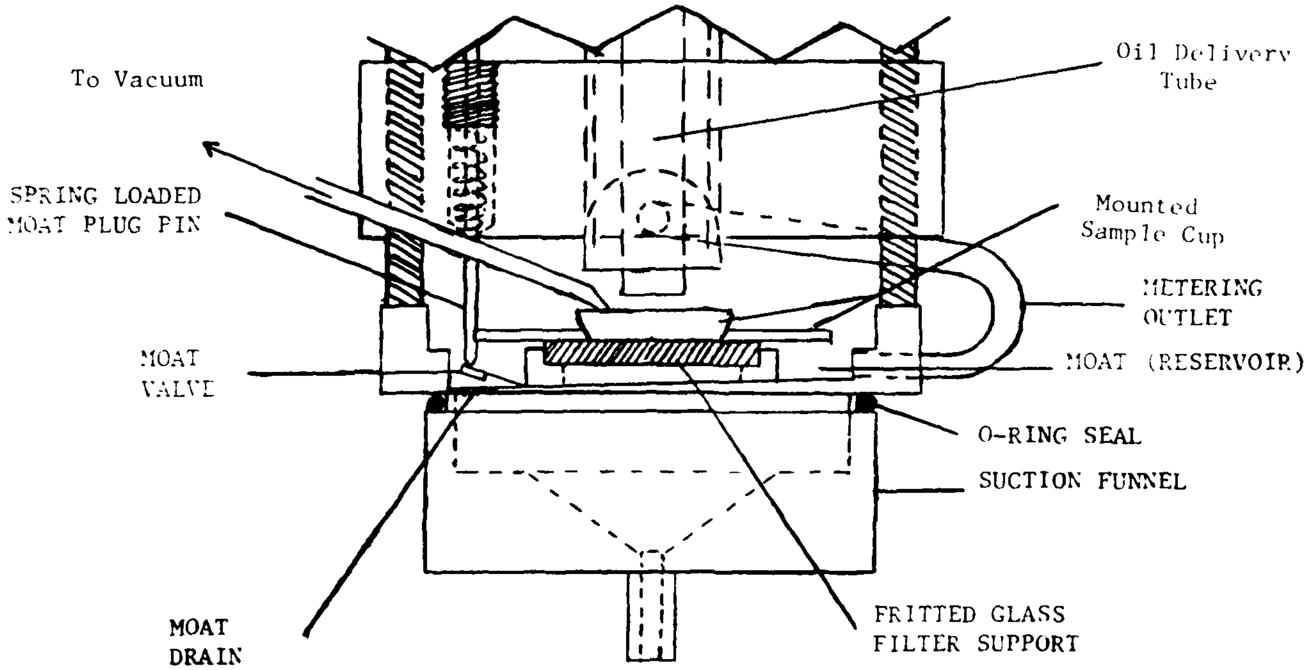

Figure 8-3
Sketch of QFA Modification
for Bulk Analysis

Tradeoff studies lead to choice of a two-unit system. The two-unit concept offered several advantages; separate units provide greater portability, improved maintainability and lower development cost. As the design evolved, Unit 1 came to include the sample handling and x-ray analysis systems together with the data collection microprocessors and memory buffers. Unit 2, the HP85 professional computer, performs all the necessary calculations and contains the print-out, lighted display, and permanent data storage. The two-unit system is pictured and diagrammed in Figures 8-4 and 8-5. In their final form, both units are easily portable, as illustrated by the mass properties summary, Figure 8-6.

We sought to minimize the possibility of operator error by making the OWAX unit simple to operate and by incorporating several "operator-proof" features. In running the OWAX, all the operator needs to do is to add oil, input the sample ID, and upon instructions from the computer, advance the filter holder. Thus, an operator needs no special knowledge, and can be trained in a matter of minutes. Maintenance of the unit is also very simple; the user need only drain the waste reservoir and refill the solvent container. Figure 8-7 summarizes the operator's sequence and Figure 8-8 shows the cue lights which provide instructions during an analysis run.

To help avoid damage to the instrument from operator error, the OWAX is equipped with several fail-safe features. When the oil metering block is in the up position, the lid to the sample chamber can't be opened, preventing oil spillage in the interior of the analysis box. There is also a guide in the oil funnel to limit overfill, and a moat drain to dispose of any spill-over as a result of inadequate filtration. A swirling solvent rinse provides a general clean-up, and assures that all the particles to be analyzed are captured on the filter. Automatic metering guarantees that the sample size is uniform, and avoids introducing operator errors in measurement. Finally, the filters are pre-mounted in 35mm slide mounts to reduce the amount of handling by the operator and help ensure that the filters remain clean.

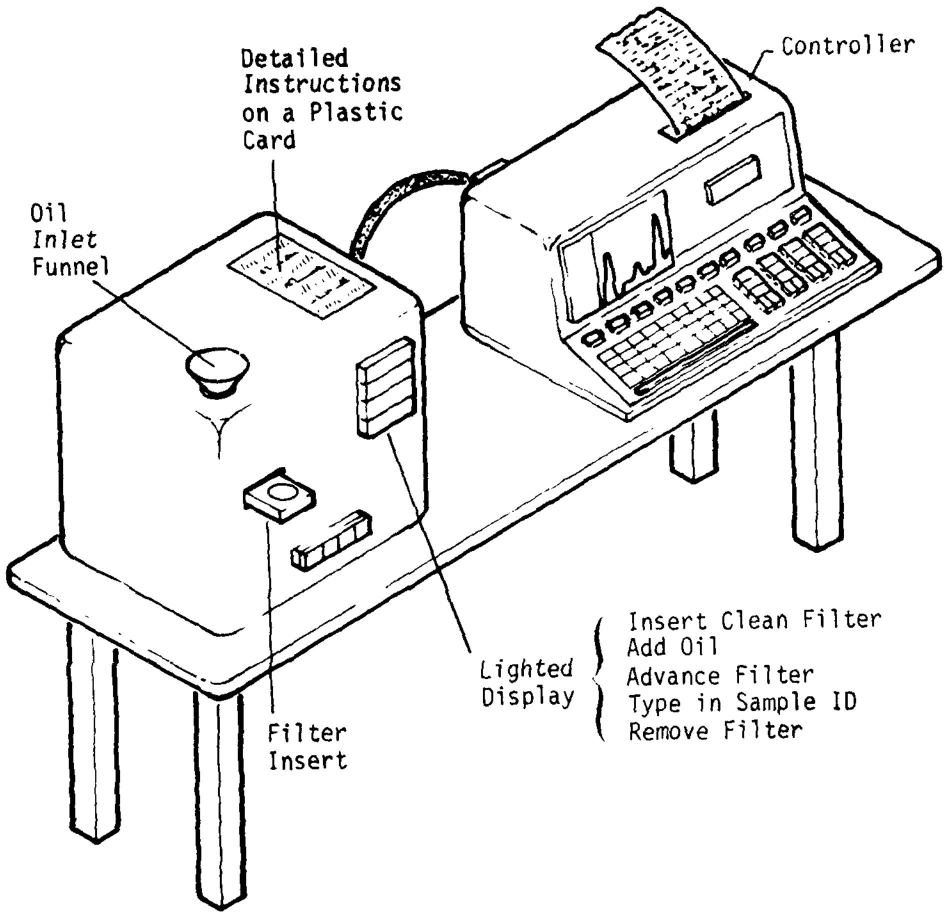

Figure 8-4
Schematic Concept of Two-Unit
Sample Handling System

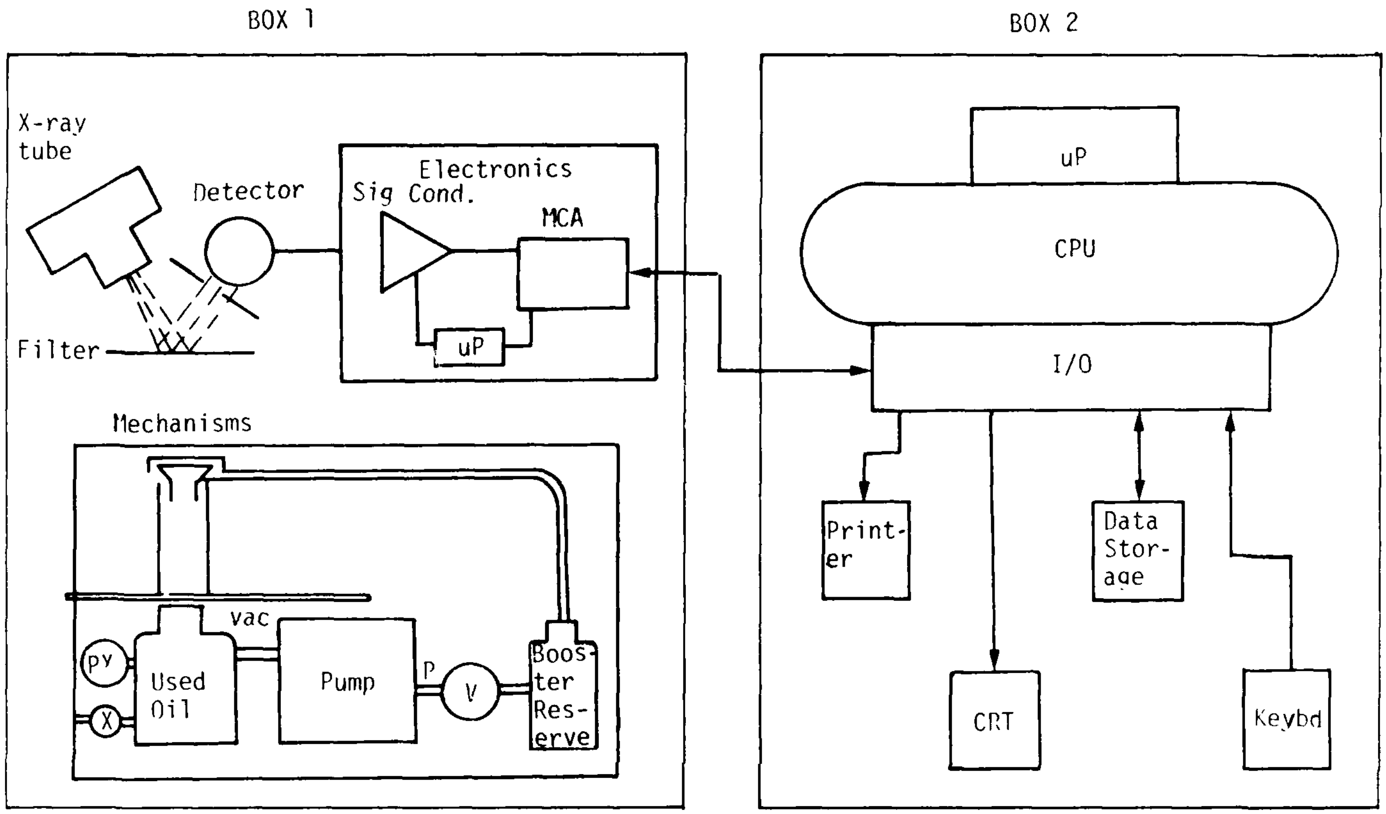

Figure 8-5

Concept Schematic:
Two-Box Concept

MASS PROPERTIES SUMMARY

BOX 1		BOX 2	
DEVICE CONTROLLER		ENCLOSURE	15-16
COMPUTER		PXRFS ELECT.	6-8
KEYBOARD		ADD'L ELECT.	2-4
TAPE DRIVE		POWER COND.	2-5
CRT DISPLAY		X-RAY TUBE	3-7
PRINTER (32 CHAR)		PUMP	2-6
		PLUMBING (DRY)	1-3
		MECHANISMS	2-4
TOTAL WEIGHT:	19.8 LBS. (9 KG)	TOTAL WEIGHT:	33-53 LBS (15-24 KG)
SIZE:	17" x 18" x 7"	SIZE:	17" x 18" x 10"

Figure 8-6
Mass Properties Summary

MARTIN MARIETTA

OPERATOR'S SEQUENCE

- REMOVE PREVIOUS FILTER; INSERT NEW ONE; LOWER PROPORT, MECH.
  - SHAKE UP OIL BOTTLE AND POUR INTO FUNNEL
    - ENTER SAMPLE I.D.
      - RAISE PROPORT, MECH. AND ADVANCE FILTER
        - INSPECT RESULTS

- HOUSEKEEPING

  DRAIN OIL RESERVOIR

  REPLENISH RINSE/BOOSTER LIQUID

Figure 8-7
Operator's Sequence

MARTIN MARIETTA

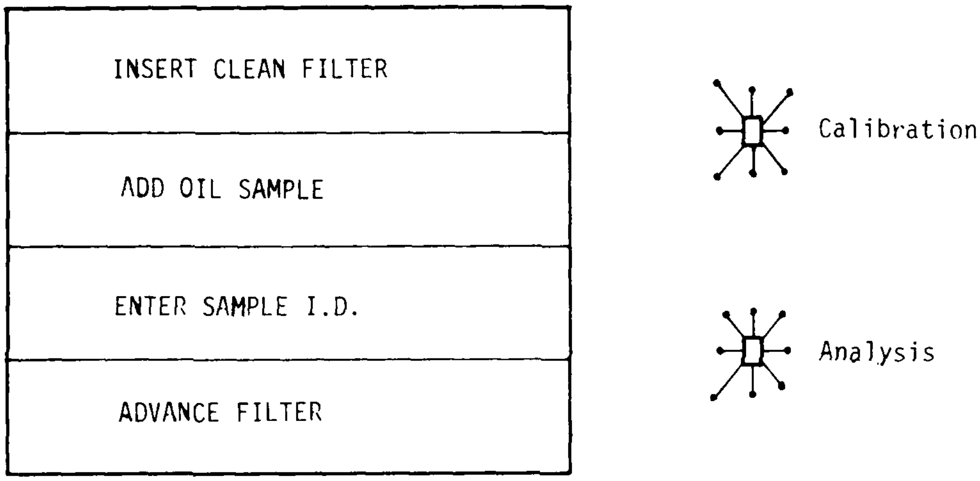

Figure 8-8
Operator Viewpoint

The last aspect of system optimization is the efficiency of the analysis sequence. By overlapping functions, as illustrated in Figure 8-9, the total time needed for a complete analysis is greatly reduced. The two-unit concept is helpful in this area, as is the implementation of the computer. The time-line, Figure 8-9 illustrates the overlapping functions. The average time for a complete analysis is five to ten minutes, varying according to how dirty the oil sample is, as older oils contain more polymeric sludge and take longer to filter. Since the samples received from JOAP were not identified as to which 7808 lubricant each contained, it was not possible to determine how various additive packages differ in the amount of sludge formed. In its present form, the OWAX maximizes accuracy and efficiency while minimizing the amount of operator effort.

PARALLEL FUNCTIONALITY

BOX 1	STEP	BOX 2
X-RAY CAL TARGET	(A)	INITIATE AUTO-CAL; UPDATE HISTORY
FILTRATION OF SAMPLE	(B)	ENTER SAMPLE IDENT.
X-RAY SAMPLE	(C)	INITIATE CLEAN-UP
CHANGE FILTER	(D)	ANALYZE DATA AND RECOMMENDATION

Figure 8-9
Parallel Functionality for Maximum Efficiency

MARTIN MARIETTA

AD-A118 477 MARTIN MARIETTA DENVER AEROSPACE CO F/G 21/5
OIL WEARMETAL ANALYSIS BY X-RAY (OWAX).(U)
MAY 82 B C CLARK, B J COOK F33615-80-C-2071
UNCLASSIFIED MRC-82-509 AFWAL-TR-82-2020 NL

2 OF 2
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118477

9. Feasibility of a Portable Wearmetal Analyzer

The feasibility assessment for this instrumentation revolves around several issues, ranging from the reliability and availability of individual hardware components to the "scientific" questions as to what is really being measured and what should be measured.

Equipment

Every effort has been made during the course of both this study and the internal development effort to consider hardware components which are rugged, reliable, and durable. All approaches have endeavored to be low-risk and based upon sound engineering practices and experience. This has obviously eliminated certain alternative, high-risk approaches. The original motivation was the perceived need of some type of portable wearmetal analysis instrumentation on a very timely basis. Our recommended design fulfills these objectives.

Not only does a "brassboard" demonstration model of this instrumentation now exist, but all components are either of proven design or currently available commercially. In Table 9-I, we summarize the heritage of all major component systems. It will be seen that this design is a blend of commercial, space, and laboratory technology. Economic considerations have been very much a factor in this blend, as has also the portability factor.

Specific benefits to this work have included the miniature x-ray tube and power supply developed by Martin Marietta for NASA's Langley Research Center. Another benefit stems from the extraordinary investment by commercial industry in design and manufacture of small, self-contained computer/controller devices. We have exploited their investment by limiting the instrument's "smart" functions to input/output interfacing, and control, and by providing a computer-compatible RS-232 serial interface.

Table 9-I. Feasibility Assessment

Subsystem	Heritage
X-ray tube	Water Quality Analyzer (NASA)
Detector	Commercial
Signal Conditioning Electronics	PXRFS
MCA, Microprocessor	PXRFS
Controller Interface	Martin Marietta IR&D
Controller/Analyzer (computer, printer, display)	Commercial
Filter Media	Commercial
Filter Mechanism	New, Martin Marietta IR&D

A very comprehensive study of filtration and booster methods for oil filtration has considerably extended the state-of-the-art as it existed when this study began. Materials compatibilities problems, essential criteria for long-term reliable operation, have also been carefully addressed during this investigation.

Sensitivity

A key question has been the sensitivity of x-ray fluorescence in the parts per million range necessary for useful analysis of jet engine lubricant. This problem has been solved for a portable instrument via the filtration technique. Although it is now known that filtration does not capture all the metal atoms in typical oil samples, we have shown that every sample so far submitted to us has, without exception, revealed one or more elements of interest. On the other hand, we have also demonstrated in one case (sample supplied by Lt. Col. B. B. McCaa, JOAP-TSE) the detection of several metals in a series of oil samples taken prior to a mechanical failure - in which case the spectrometric results were essentially null. Generally, the x-ray technique detects about half a dozen wearmetal elements in most samples. Sensitivity for iron particles greater than 1 um in diameter has been demonstrated to be better than one part per million.

Accuracy

The question of the accuracy of analysis of any of the oil wearmetal analytical techniques is one sense irrelevant because no operational technique is particle-size independent. As we showed by the standards series and sample size variation tests described in Section 2 above, a reliable calibration curve can be constructed for the x-ray technique.

The important question, however, relates to the precision with which repeated analyses of the same engine over a period of time can reflect normal wear trends and detect anomolous increases in wearmetal debris. These data do not yet exist for x-ray fluorescence analysis. Although there is no basis for assuming deficiencies of the method in this regard, a series of tests which are proposed for the purposes of more fully investigating the differences between current SOAP technique and x-ray technique will answer this question as well. Most importantly, the proposed methodology must be evaluated for success in pinpointing incipient engine failures as well as any propensity for falsely indicating failures in times of normal operation.

Correlation with SOAP Analyses

Over two dozen samples, some provided by AFWAL/POSL and the majority provided by the JOAP office at Pensacola, NAS, have now been analyzed by the filtration x-ray technique. In Figure 9-1, we plot net x-ray peak intensities for the element iron versus the SOAP analysis for Fe in each sample. Crude trend agreement can be seen, but there is no one-to-one correlation between values. Some clustering is apparent (for example, the four samples at coordinates 13 ppm, 300 counts). It is likely that particle size distributions of wearmetal debris are characteristic for each different engine type. Since these samples represent a variety of aircraft engines, it is not necessarily surprising that correlations are weak since the x-ray filtration technique emphasizes large particles while SOAP detects only dissolved metal and small particles. Similar results are obtained with other elements; an example is chromium, Figure 9-2.

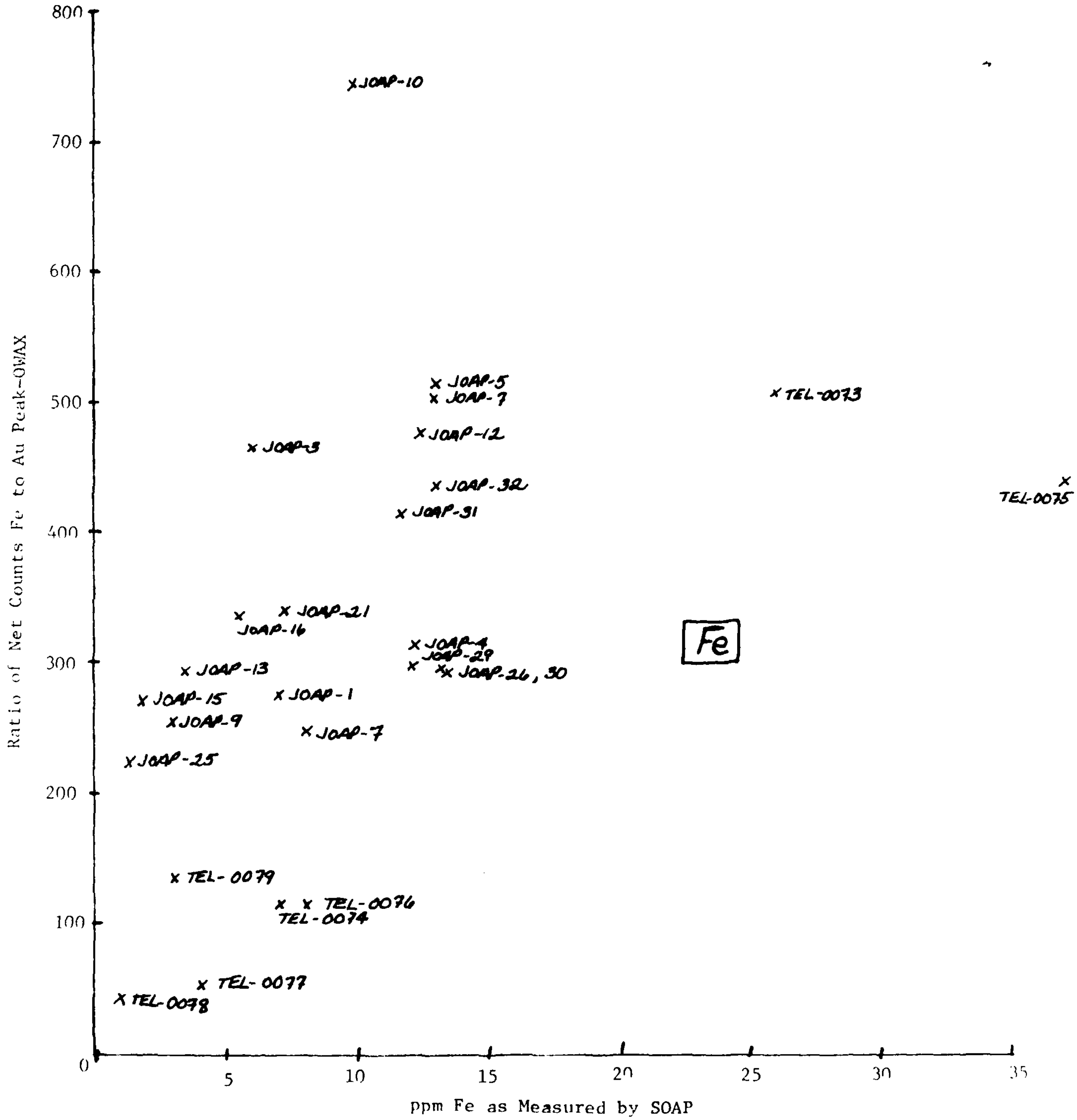


Figure 9-1
OWAX Fe Concentrations vs.
SOAP Values

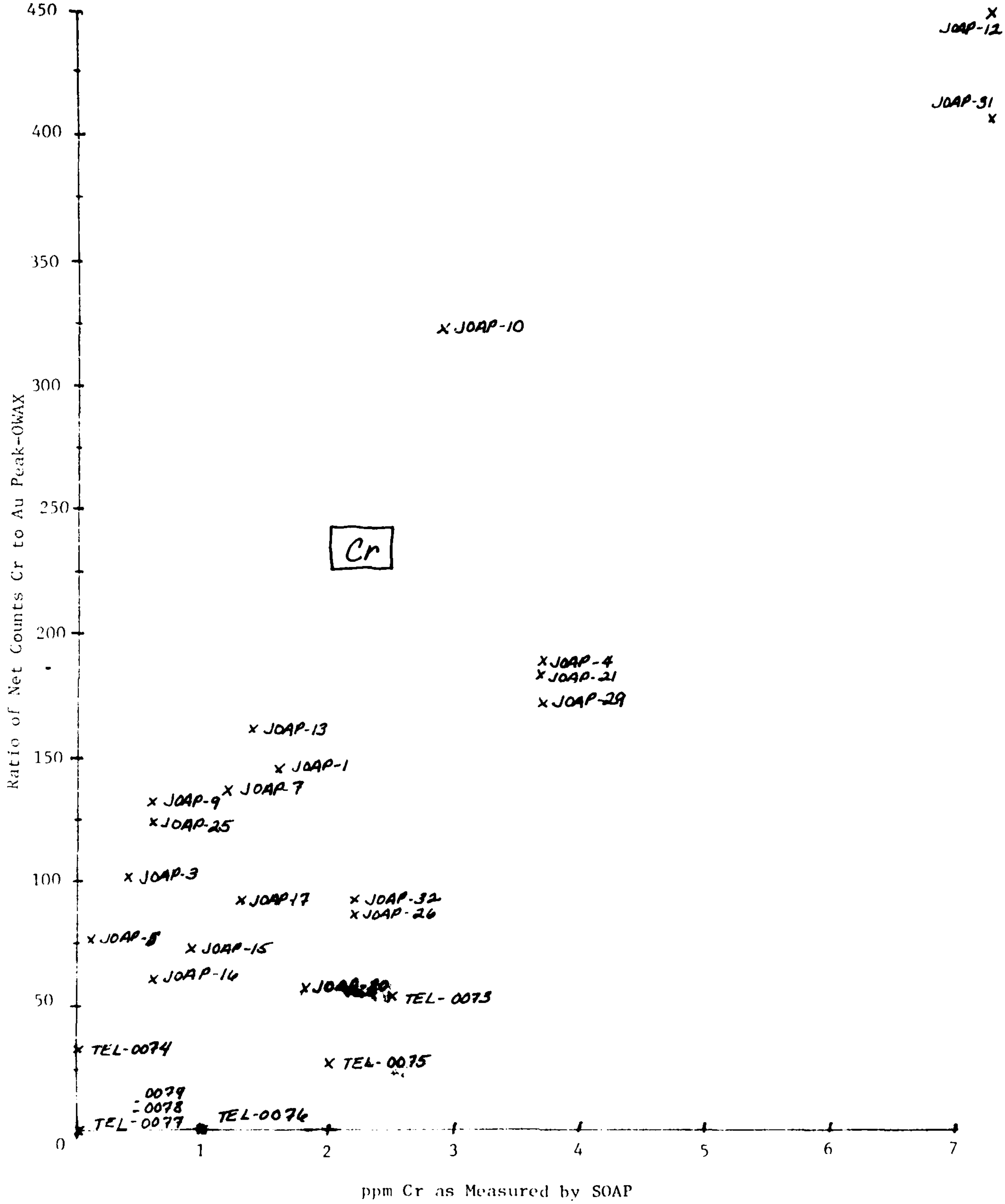


Figure 9-2
OWAX Cr Concentrations vs. SOAP Values

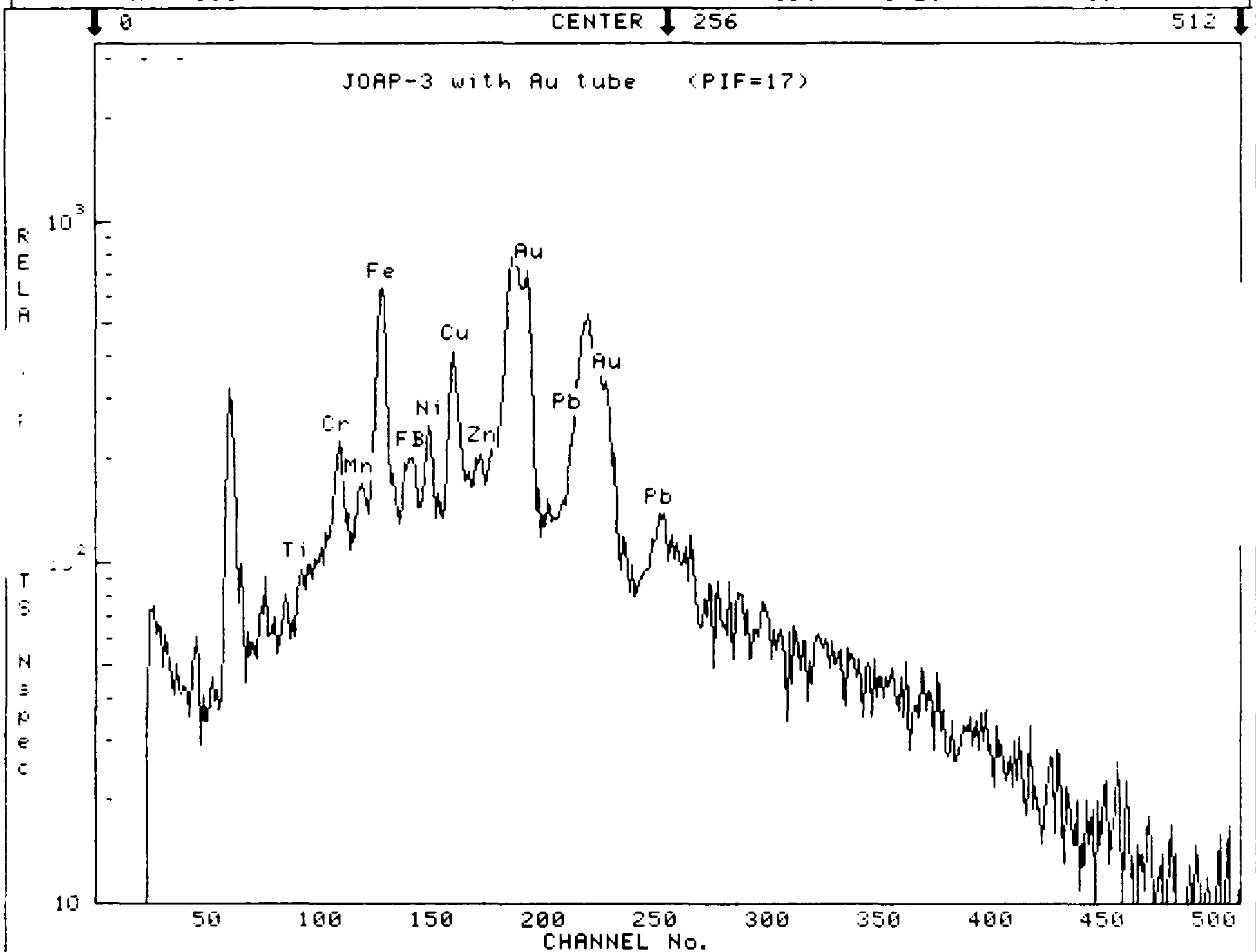
Of special interest are cases where x-ray detects an element which SOAP does not, and vice-versa. At this point, it would be dangerous to draw premature conclusions of the significance of this fact without follow-up studies. Nonetheless, a few examples should be considered. In our spectra of samples JOAP-3 and JOAP-5, Figures 2-4 and 2-5, clear indication of the metal Cr is present. SOAP, however, analyzed only 0.4 and 0.1 ppm Cr, respectively. On the other hand, SOAP measures 1.0 ppm Zn in JOAP-5, while x-ray analysis indicates a negligible presence of this element. In sample JOAP-16, x-ray sees a quite significant Zn peak, while SOAP reports only 0.3 ppm. For JOAP-31, x-ray sees the high indicated Cr and Fe, and some Zn (0.9 ppm according to SOAP), no evidence of Cu (6 ppm SOAP), and a weak, but positive Ti peak (0 ppm SOAP). In sample JOAP-25, SOAP indicates low levels of Cr, Fe, Cu, and Zn (0.6, 1.3, 1.4, 1.0 ppm); x-ray sees relatively much stronger signals from Cr, Fe, and Cu, as well as indications of Mn and Ni, Figure 9-5. The element Fe is seen by the x-ray technique, as well as SOAP, in every sample tested, with the exception of TEL-0077, a sample of unused engine oil.

The samples tested to date are undocumented with respect to aircraft engine type and history. Clearly, controlled tests would be very valuable to establish the degree to which SOAP and x-ray analyses can be correlated on the basis of engine types and time since overhaul. Since there is every reason to believe that the x-ray filtration method, being particularly sensitive for large particles, and hence for primary wear debris, will be just as effective or even more effective than SOAP, a portable x-ray instrument could be used for rapid deployment operations.

As originally suggested to us by P. Centers of AFWAL/POSL, once deployment operations were indicated, supplementary x-ray data could be taken during routine SOAP analysis. If necessary, special pre-deployment samples could be taken and analyzed. During remote site operations, the portable instrumentation would monitor lubricant wearmetal and detect abrupt changes in level or trend. In this relatively unusual event, a decision could be made to either use the x-ray data alone or to fly a sample to a station with SOAP instrumentation. With operational experience, the x-ray technique could be shown to be a highly reliable proxy for SOAP analyses.

JOAP-3 with Au tube 1

	Si(Li)	Cd-109	RunID: OW-366
STORED UNDER: SPF08C			
SPECTRUM #: 17			OPERATOR: bjc
CHANNELS : 512			START : 08:30:57
OFFSET : 0			DATE TAPED: 102881
TOTAL COUNT:	51853 COUNTS	COUNT RATE:	259.3 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	782 COUNTS	CLOCK TIME:	200 SEC



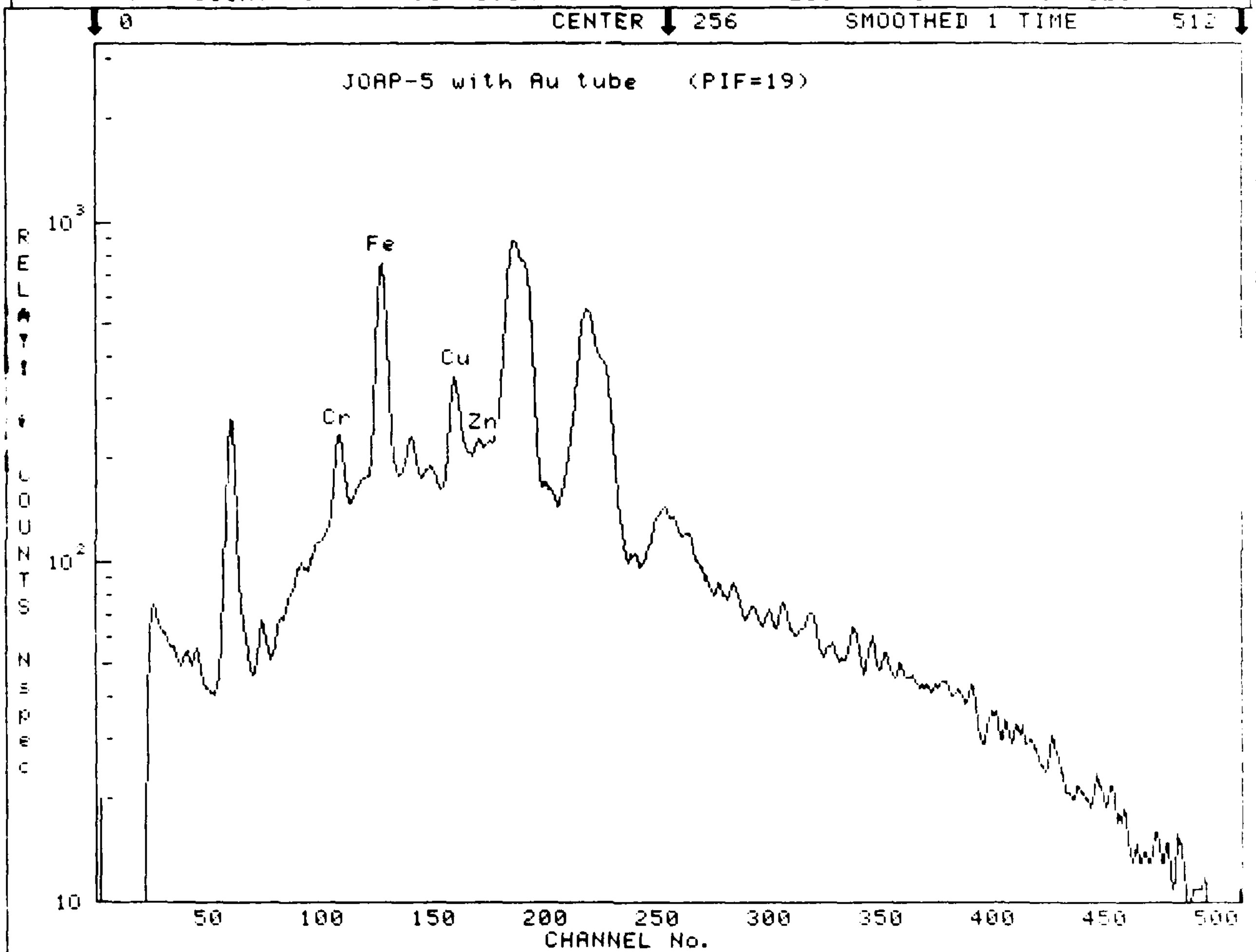
COMMENTS TO DATE

3.5 ml oil on Tyrann. With x-ray tube. In air.

Figure 9-3
Comparison of OWAX and SOAP Results,
JOAP-3

JOAP-5 with Au tube

	Si(Li)	Cd-109	RunID: OW-368
STORED UNDER:SPF08C			
SPECTRUM #: 19		OPERATOR: bjc	
CHANNELS : 512		START : 08:39:20	
OFFSET : 0		DATE TAPED: 102881	
TOTAL COUNT:	58429 COUNTS	COUNT RATE:	292.1 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	913 COUNTS	CLOCK TIME:	200 SEC



COMMENTS TO DATE

3.5 ml oil on Tyrann. With x-ray tube. In air.

Figure 9-4
Comparison of OWAX and SOAP Results,
JOAP-5

JOAP-25 with Au tube

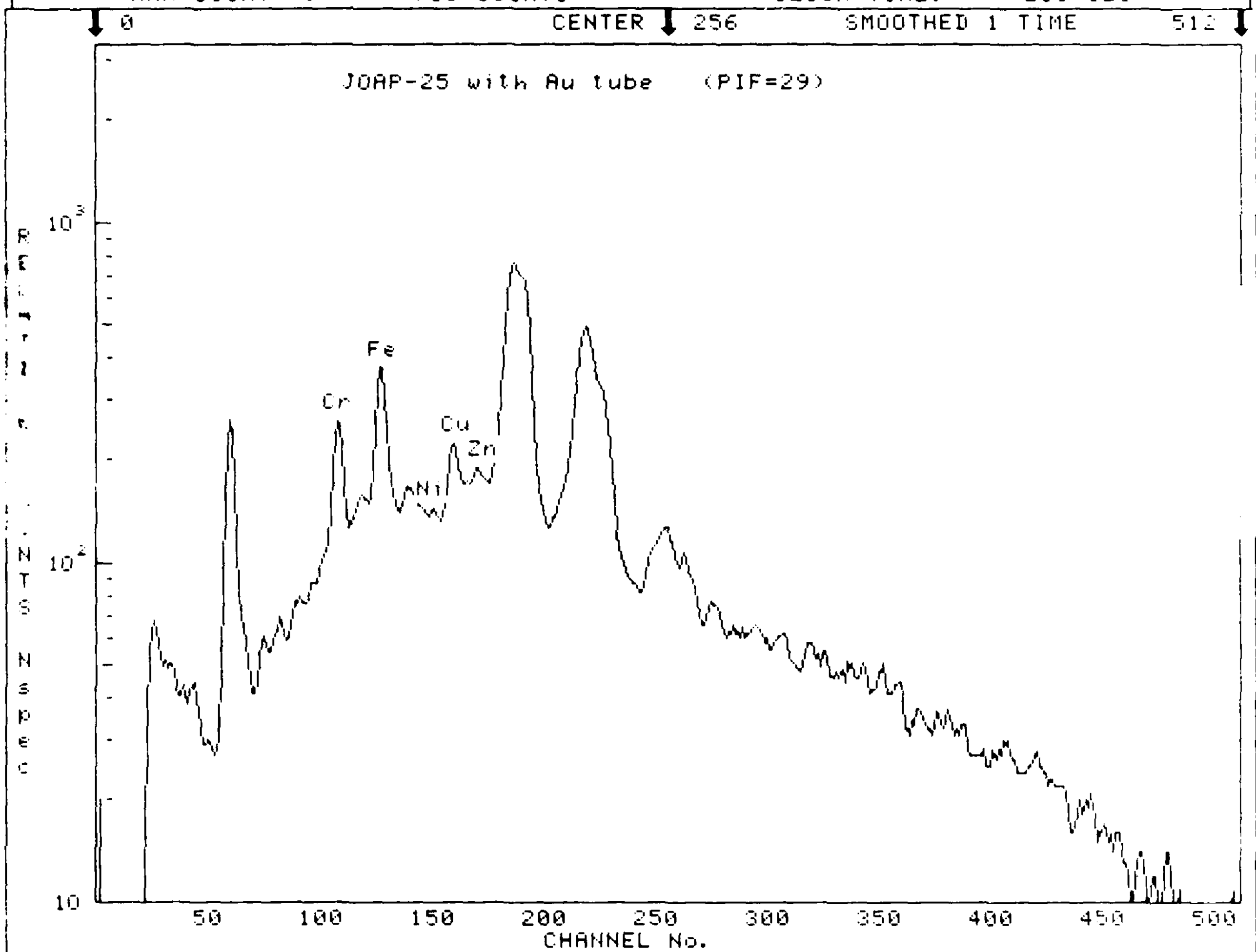
Si(Li)	Cd-109	RunID: OW-378

STORED UNDER:SPF08C
SPECTRUM #: 29
CHANNELS : 512
OFFSET : 0

OPERATOR: bjc
START : 09:36:08
DATE TAPED: 102881

TOTAL COUNT: 48401 COUNTS
INTEGRATE PEAK: 0 COUNTS
MAX COUNT : 755 COUNTS

COUNT RATE: 242.0 CPS
LIVE TIME : 0 SEC
CLOCK TIME: 200 SEC



COMMENTS TO DATE

3.5 ml oil on Tyrann. With x-ray tube. In air.

Figure 9-5
Comparison of OWAX and SOAP Results,
JOAP-25

CONCLUSIONS AND RECOMMENDATIONS

This study, and auxiliary developments, have demonstrated the feasibility of a portable x-ray fluorescence based system for particulate wearmetal analysis in aircraft engine oils. The system's advantages are:

- man-portable
- fast analysis time
- easily calibrated
- computer controlled
- computerized data analysis and storage
- analysis emphasizes particulate debris
- low power consumption; no gases or water cooling needed
- analysis of Fe, Ti, Cu, Cr, Zn, and Ni
- bulk analysis of "dirty" oils also possible

The system's disadvantages are:

- liquid nitrogen required for operation
- analysis for Ag difficult; analysis for Mg, Al unproven
- dissolved metals not analyzed; imperfect correlation with SOAP

A major unknown is whether this system can anticipate imminent engine failures to the same degree of success as the present SOAP program. Since most wear mechanisms produce large particles initially, this filtration technique could be superior to SOAP in some or most cases, provided that sampling at the engine picked up the larger particles. To date, one documented example has been conclusively demonstrated. (AH-1S Helicopter oil sample supplied by Lt Col B. B. McCaa, JOAP, and tested on 10 December 1981.)

As a result of these pathfinder investigations, we have three recommendations for future work:

1. Analyze a large number of engine oil samples over a period of time, establishing a preliminary data base for a variety of selected aircraft.

2. Conduct development to assess capability of measuring silver, magnesium, aluminum, and silicon in engine oil samples. Also determine feasibility of implementing this capability into portable instrumentation.

3. Build a deliverable Oil Wearmetal Analyzer by X-ray (OWAX) instrument for evaluation in an appropriate military setting.

APPENDIX A

Martin Marietta OWAX Brassboard

The Oil Wearmetal Analysis by X-ray (OWAX) system is a portable unit which analyzes particulate metals in aircraft engine oils. It provides immediate information, requires no elaborate sample preparation or special training for the operator, and can record the history of each engine tested. Using x-ray fluorescence spectrocopy, the OWAX both produces and interprets a spectrum, then calculates the concentration of metals present in a sample.

The OWAX system has two parts; the main filtration/data taking unit and the Hewlett-Packard 85 desktop computer. The main unit, diagrammed in Figure A-1, contains the system electronics, the x-ray tube and proportional counter, and the sample filtration system. The computer connects to the main unit via an RS232 interface. Figure A-2 shows the OWAX in use, and Figure A-3 pictures the interior of the analysis unit.

The filtration system uses a small diaphragm pump to suction filter oil through a 0.45 um membrane filter mounted in a 35mm slide mount. Other components of the filtration system include the sample metering/filtering block, solvent and waste bottles, vacuum line solenoid valves, and filter holder. There is also a port for an auxiliary vacuum pump.

The electronics consist of an RCA 1802 Microprocessor which controls three input/output ports. One port is in control of the filtration system hardware, another controls data input and analysis, and the third connects the microprocessor with the RS232 computer interface. In addition, the proportional counter has a high voltage supply, and a signal conditioner which connects to the microprocessor. The unit has two power supplies, one 28 VDC and one +5 and +12 VDC dual supply. Each supply can operate from a wide range of power sources (90 to 250 VAC at 40 to 440 Hz).

The Hewlett-Packard 85 is a compact, desktop computer which operates in BASIC. It has a 32,000 byte memory and built-in graphics capabilities for both a screen and a thermal printer.

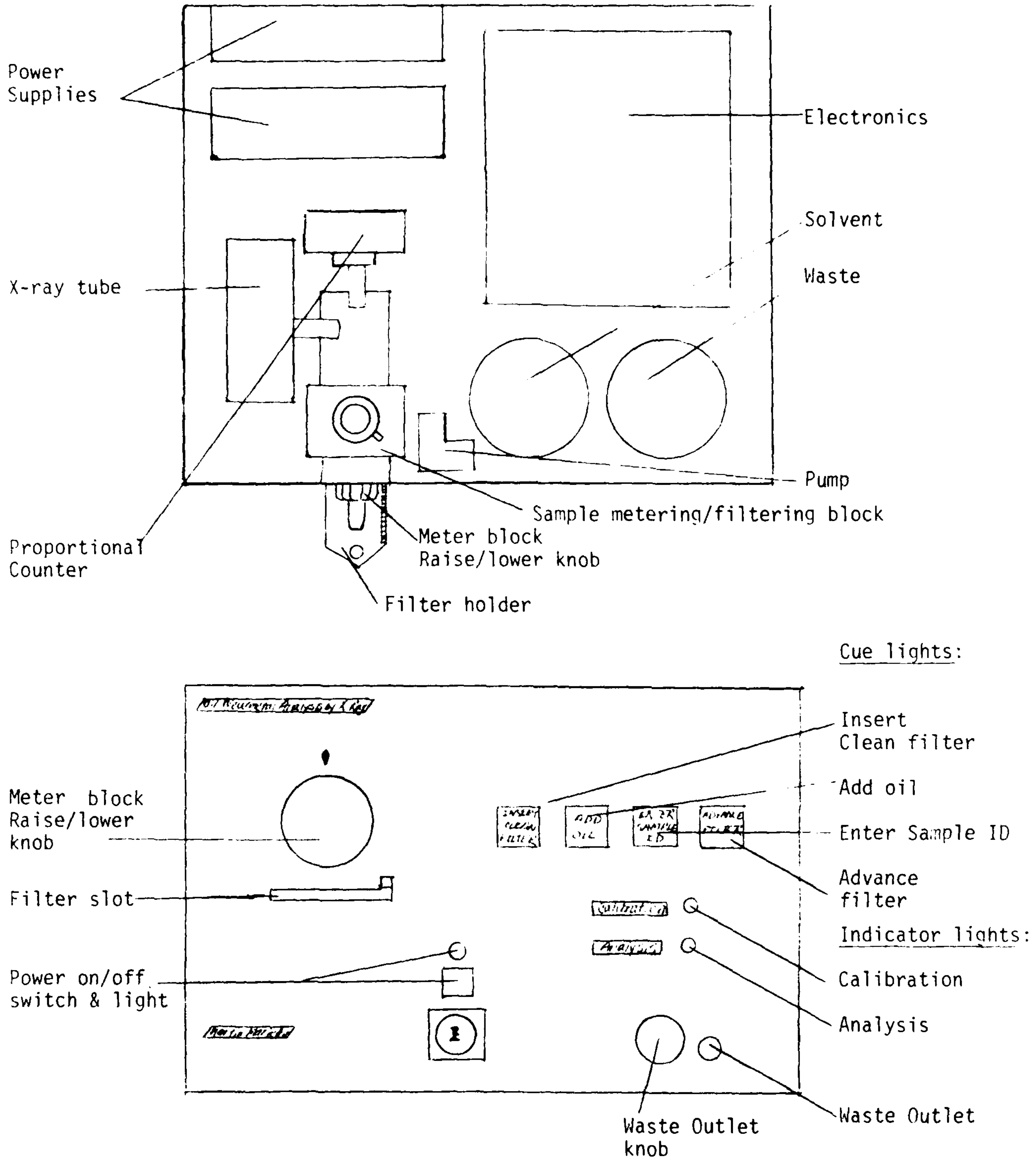


Figure A-1

OWAX Analysis Unit; Diagram

Figure A-1
[illegible] in Operation

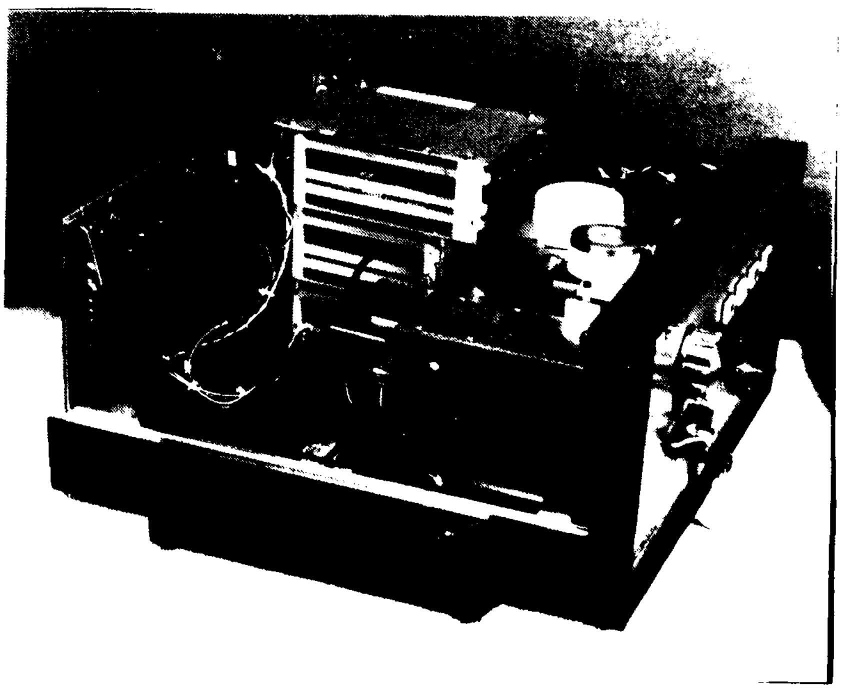


Figure A-[illegible]
Interior of [illegible]

[illegible]

During operation, the user inserts a clean filter into the filter holder and slides it into a slot in the front panel, Figure A-1. A motor pulls the filter holder into position, then the operator lowers the metering block and adds oil. Because the metering block allows any excess oil to run off as waste, it is not necessary for the user to measure the oil sample, and a uniform sample size is assured. The pump then suction filters the oil and rinses the line with a small amount of solvent. The operator raises the metering block and the motor advances the filter until it is positioned beneath the detector, ready for analysis.

The computer guides operation of the OWAX with a series of prompts to the microprocessor. The microprocessor controls power to the pump, opens and closes the solenoid valves in the solvent and vacuum lines, and sends messages to the operator via the front panel lights (Figure A-1).

After the sample is filtered, it is ready for analysis. On a prompt from the computer, the microprocessor sends power to the x-ray tube and proportional counter. When the sample is irradiated with x-rays, electrons from the inner shells of the metal atoms are ejected, and as electrons drop from higher shells, the atoms emit characteristic x-ray spectral lines. The proportional counter makes a record of the number of fluorescent x-rays being detected at each energy level. The energy indicates the identity of the metal, and the number of counts at that energy indicates the relative amount of that metal present in the sample.

As the proportional counter takes data, the OWAX electronics store it in a RAM memory. The computer then commands the transfer of the data into its own array, does mathematical analysis, and processes the array into a graphical spectrum which the user sees displayed on the screen. Calculating the relative amounts of metal present in the sample, it then provides the operator with a printout of the spectrum and metal concentrations. The time line, Figure A-4, shows the sequence of events; the total time required for filtration and analysis is between 300 and 500 seconds, depending upon the viscosity of oil and amount of impurities present.

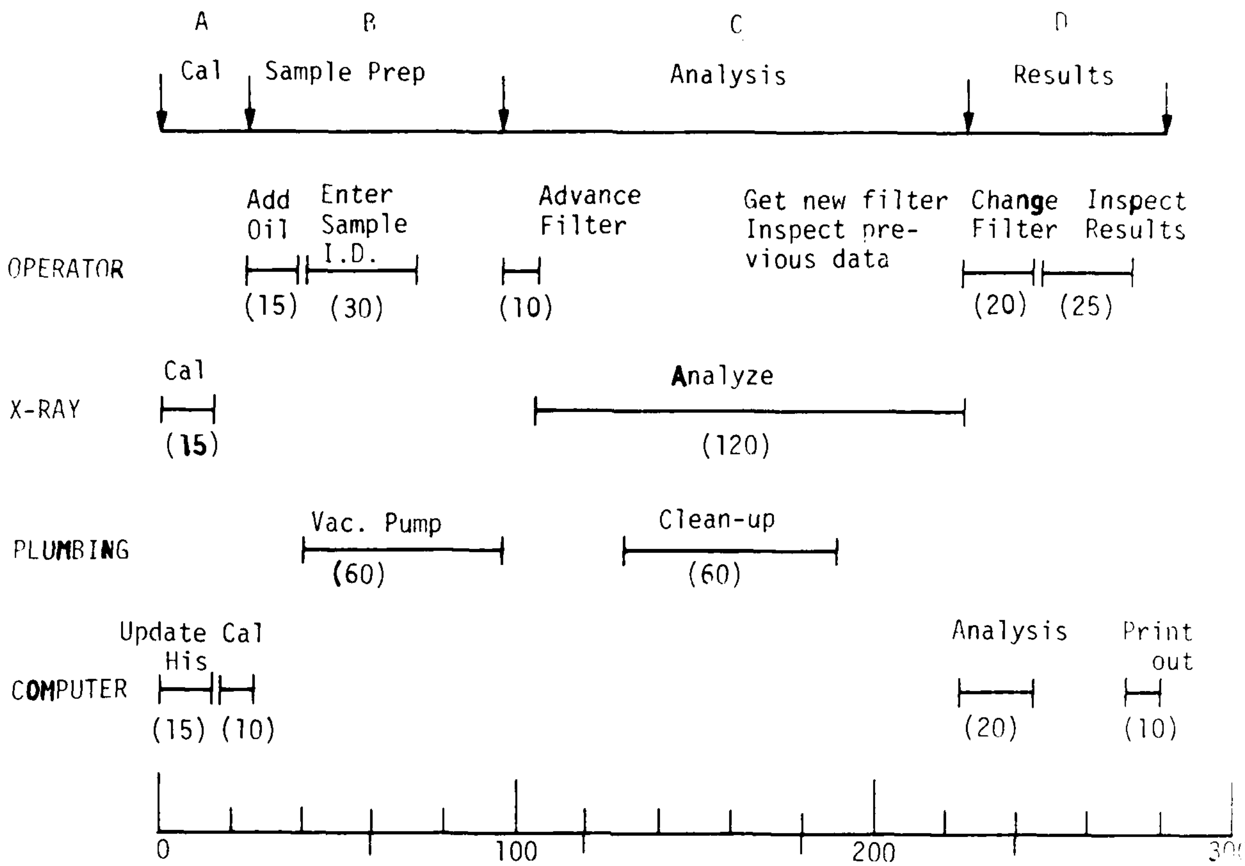


Figure A-4
OWAX Timeline

In order that results be consistent, the operator has the option of including a calibration step as part of the procedure. The metering block holds a calibration target mounted with a hinge and spring. The filter holder pushes the target out from under the detector when it advances, but the calibration target returns to its original position at other times. The calibration target allows the computer to check the signal from known targets (zinc and titanium atoms) and, if necessary, make adjustments in the overall electronic gain of the system.

Several provisions have been made to allow operation of the instrument by untrained personnel. The cover which the user opens upon adding oil cannot be opened when the meter block is in the up position, thus assuring proper filtration without danger of spillover. Since the system automatically dispenses solvent, there is no danger of adding it before the oil has finished filtering. In addition, the computer provides the operator with step-by-step instructions and explanations. Because the user need not handle the sample until the analysis is complete, all sample preparation will be uniform and the results more consistent than if operator laboratory techniques were involved. Finally, the reduced data are printed out and stored onto magnetic tape. The operator is not required to transcribe or record the data.

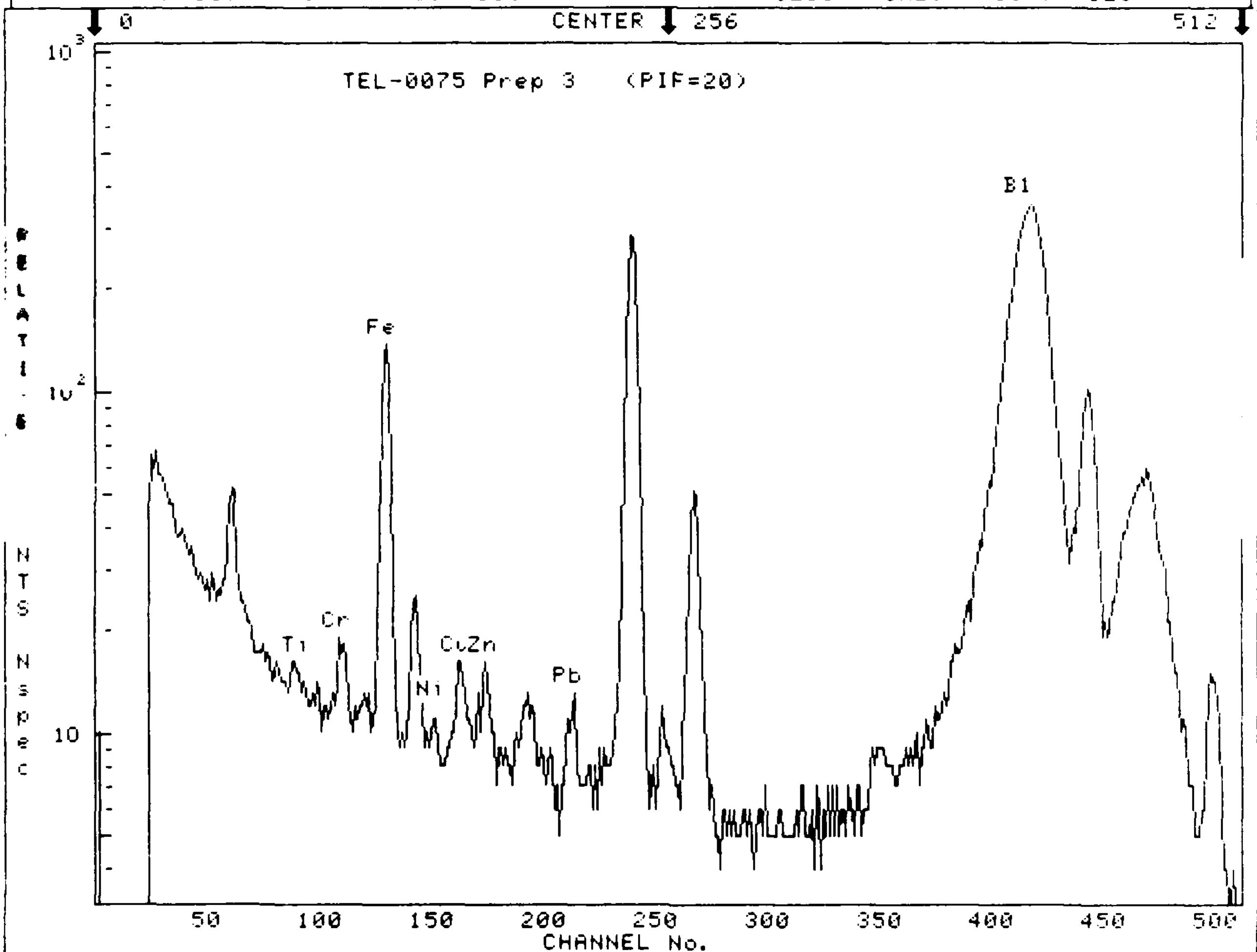
APPENDIX B

Auxiliary Spectra

The following are examples of spectra of SOAP oils analyzed by x-ray fluorescence spectroscopy using a variety of detectors, x-ray sources, and counting times.

TEL-0075 Prep 3

	Si(Li)	Cd-109	RunID: OW-213
STORED UNDER:SPF08B			
SPECTRUM #: 20			OPERATOR: bcc
CHANNELS : 512			START : 03:27:34
OFFSET : 0			DATE TAPED: 12681
TOTAL COUNT:	15755 COUNTS	COUNT RATE:	1.0 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	884 COUNTS	CLOCK TIME:	15433 SEC



COMMENTS TO DATE

same as 19, but for 80000 sec. 3 ml oil thru .4 um Nucl, with xylene

Figure B-1

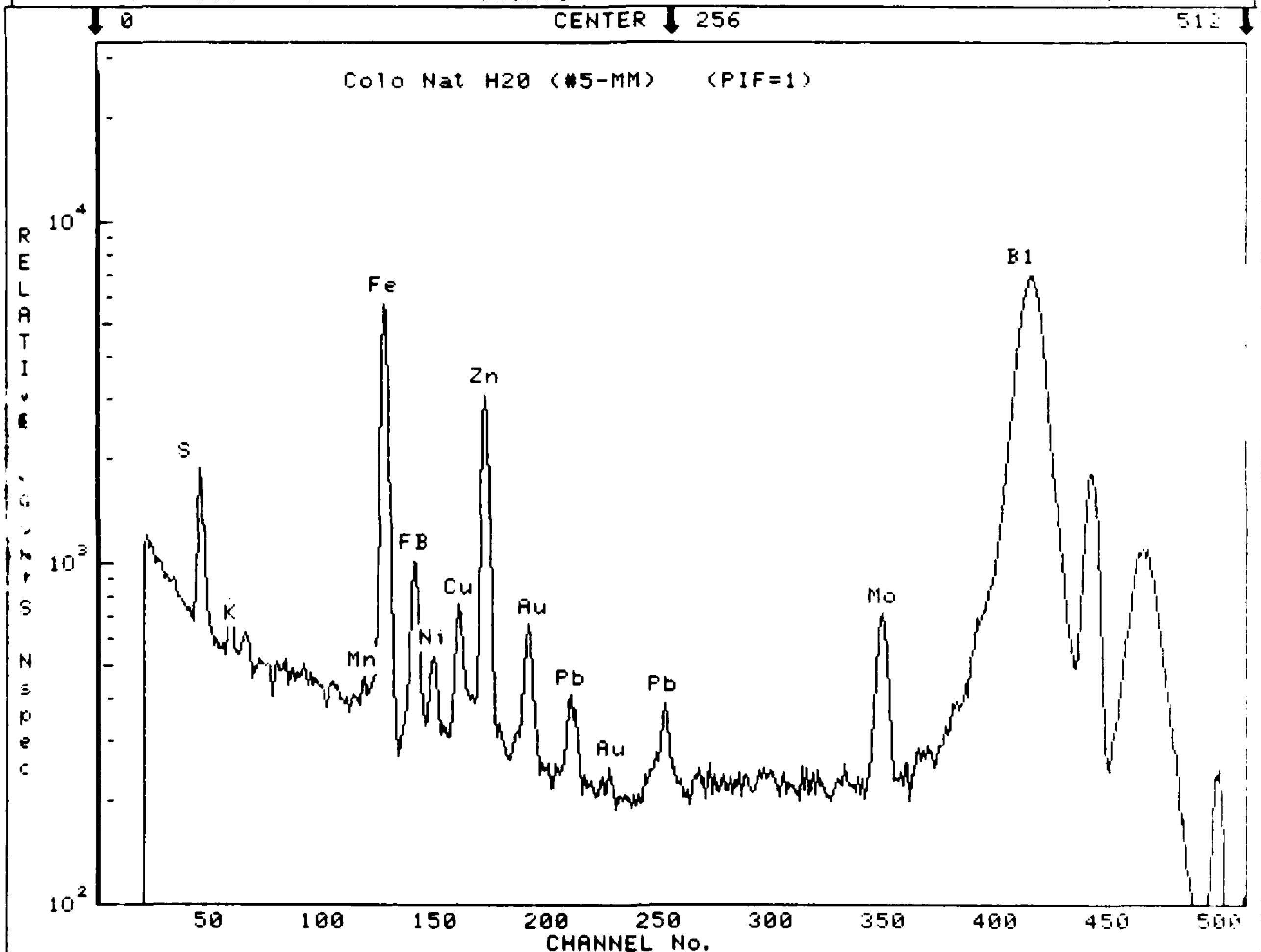
Colo Nat H20 (#5-MM) 1

Si(Li) Cd-109 RunID: WS-260

STORED UNDER:SPF03A
SPECTRUM #: 1
CHANNELS : 512
OFFSET : 0

OPERATOR: BClark
START : 11:03:30
DATE TAPED: 51680

TOTAL COUNT:	325738 COUNTS	COUNT RATE:	6.0 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	6711 COUNTS	CLOCK TIME:	54406 SEC



COMMENTS TO DATE

Bill Bodner's spec'l samp. In air on Kap. 6 cps.

Figure B-2

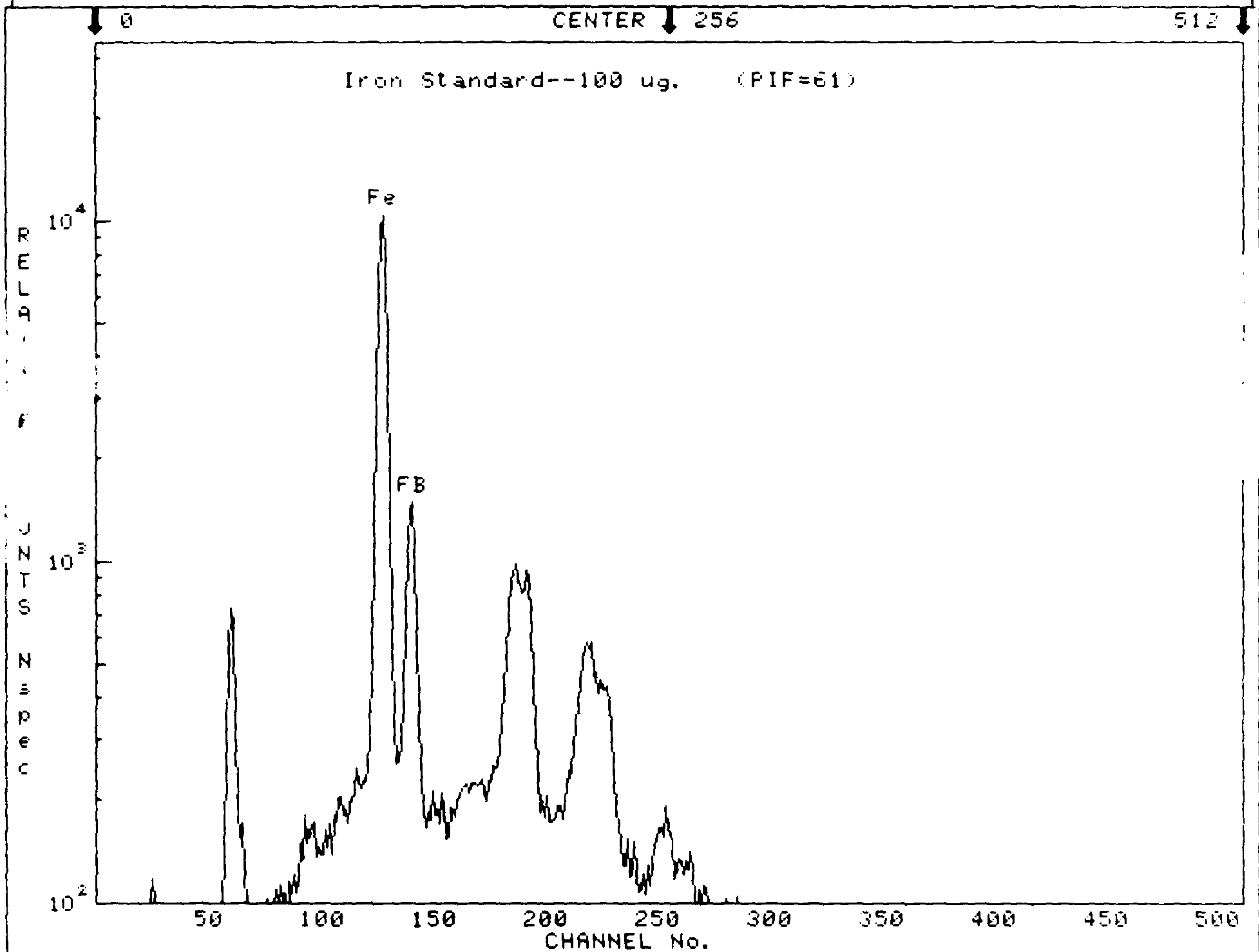
Iron Standard--100 ug. 61

Si(Li) Cd-109 RunID: OW-4.

STORED UNDER:SPF08C
SPECTRUM #: 61
CHANNELS : 512
OFFSET : 0

OPERATOR: bjc
START : 14:56:00
DATE TAPED: 11381

TOTAL COUNT:	109722 COUNTS	COUNT RATE:	274.3 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	9915 COUNTS	CLOCK TIME:	400 SEC



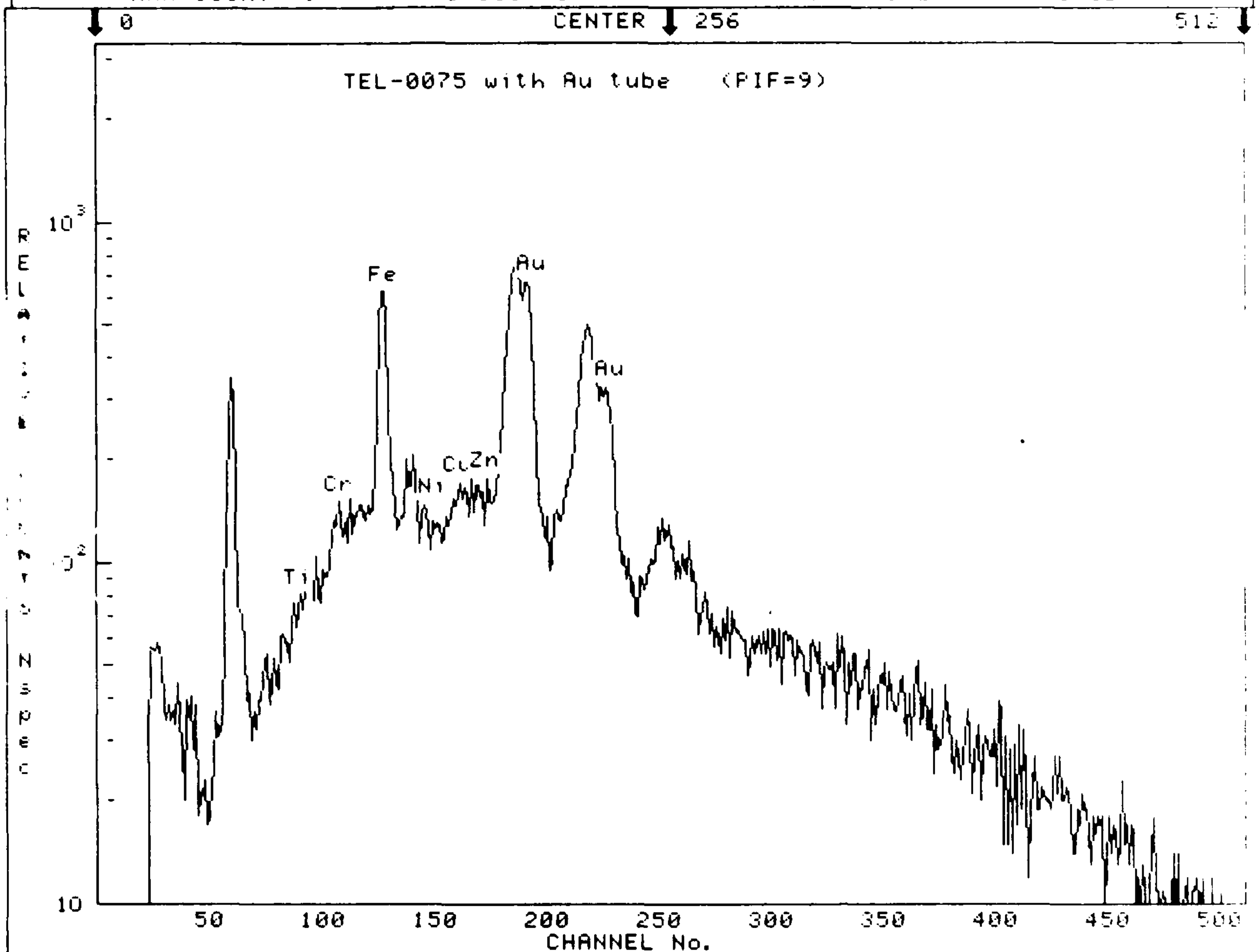
COMMENTS TO DATE

Carbonyl Fe in MIL-L-7808 on Tyrann. 1 ml 100 ppm. With x-ray tube. In ai

Figure B-3

TEL-0075 with Au tube

	Si(Li) Cd-109	RunID: OW-350
STORED UNDER: SPF08C		
SPECTRUM #: 9		OPERATOR: bjc
CHANNELS : 512		START : 10:51:05
OFFSET : 0		DATE TAPED: 102781
TOTAL COUNT:	46171 COUNTS	COUNT RATE: 230.9 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME : 0 SEC
MAX COUNT :	760 COUNTS	CLOCK TIME: 200 SEC



COMMENTS TO DATE

3.5 ml oil through Tyrann. With x-ray tube. In air.

Figure B-4

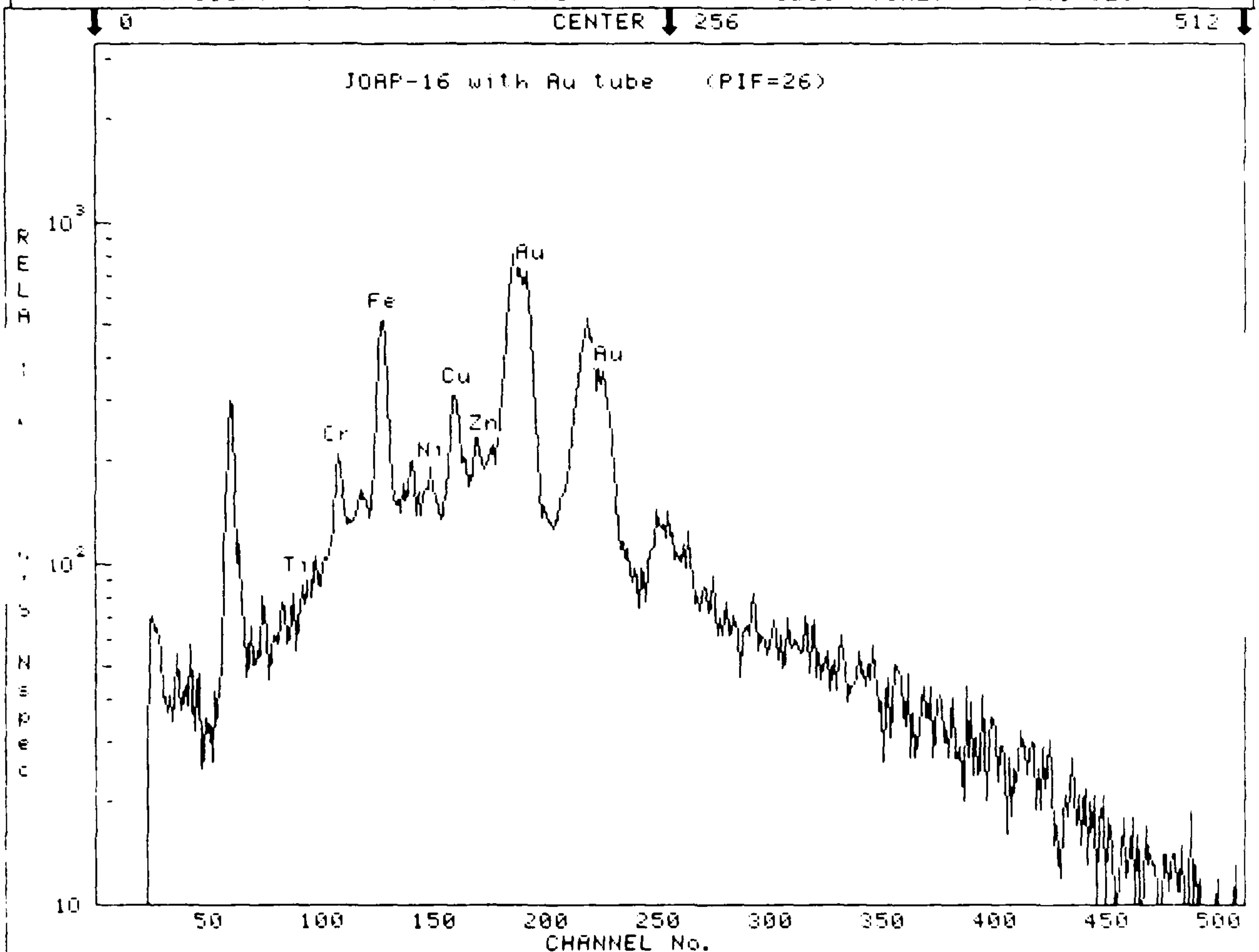
JOAP-16 with Au tube

Si(Li)	Cd-109	RunID: OW-375

STORED UNDER:SPF08C
SPECTRUM #: 26
CHANNELS : 512
OFFSET : 0

OPERATOR: bjc
START : 09:24:09
DATE TAPED: 102881

TOTAL COUNT:	50595 COUNTS	COUNT RATE:	253.0 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	796 COUNTS	CLOCK TIME:	200 SEC



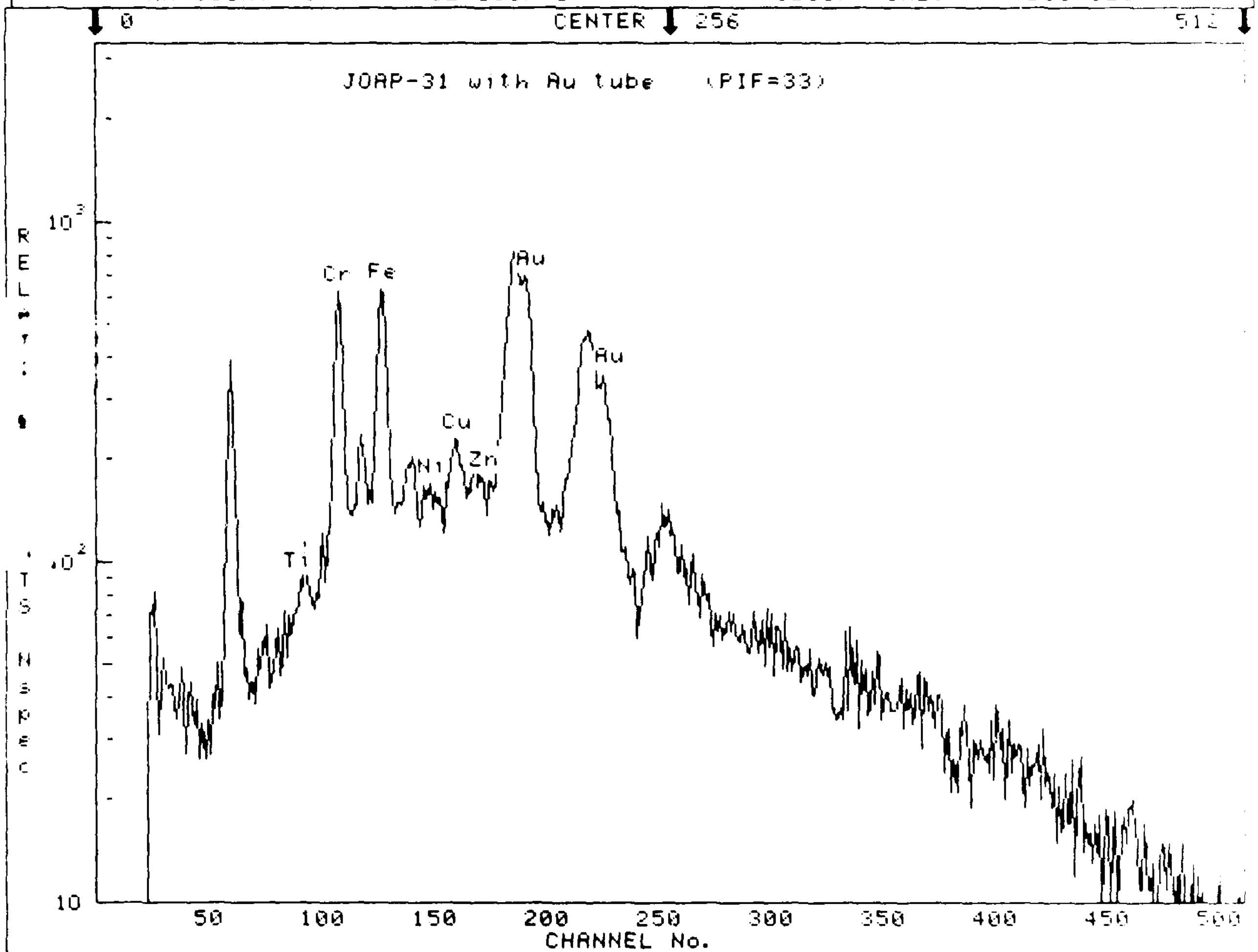
COMMENTS TO DATE

3.5 ml oil on Tyrann. With x-ray tube. In air.

Figure B-5

JOAP-31 with Au tube

	Si(Li)	Cd-109	RunID: OW-332
STORED UNDER: SPF08C			
SPECTRUM #: 33		OPERATOR: bjc	
CHANNELS : 512		START : 09:54:48	
OFFSET : 0		DATE TAPED: 102881	
TOTAL COUNT:	50389 COUNTS	COUNT RATE:	251.9 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	782 COUNTS	CLOCK TIME:	200 SEC



COMMENTS TO DATE

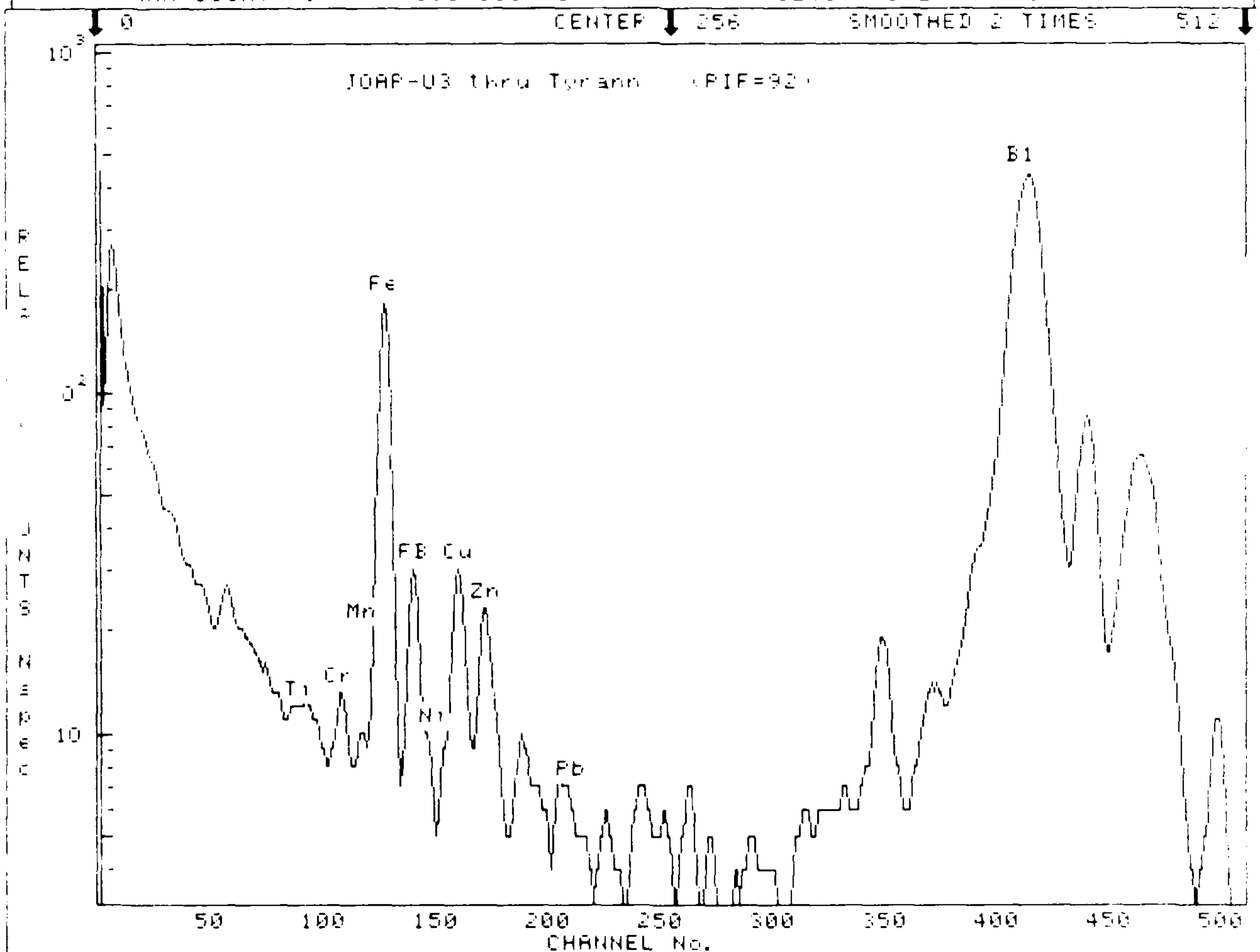
" ml oil on Tyrann. With x-ray tube. In air.

Figure B-6

JOAP-U3 thru Tyrann

Si(Li)	Cd-109	RunID: OW-282
STORED UNDER:SPF08B		
SPECTRUM #: 92		OPERATOR: bjc
CHANNELS : 512		START : 11:44:12
OFFSET : 0		DATE TAPED: 82481

TOTAL COUNT: 17197 COUNTS	COUNT RATE: 5.7 CPS
INTEGRATE PEAK: 0 COUNTS	LIVE TIME : 0 SEC
MAX COUNT : 605 COUNTS	CLOCK TIME: 3000 SEC



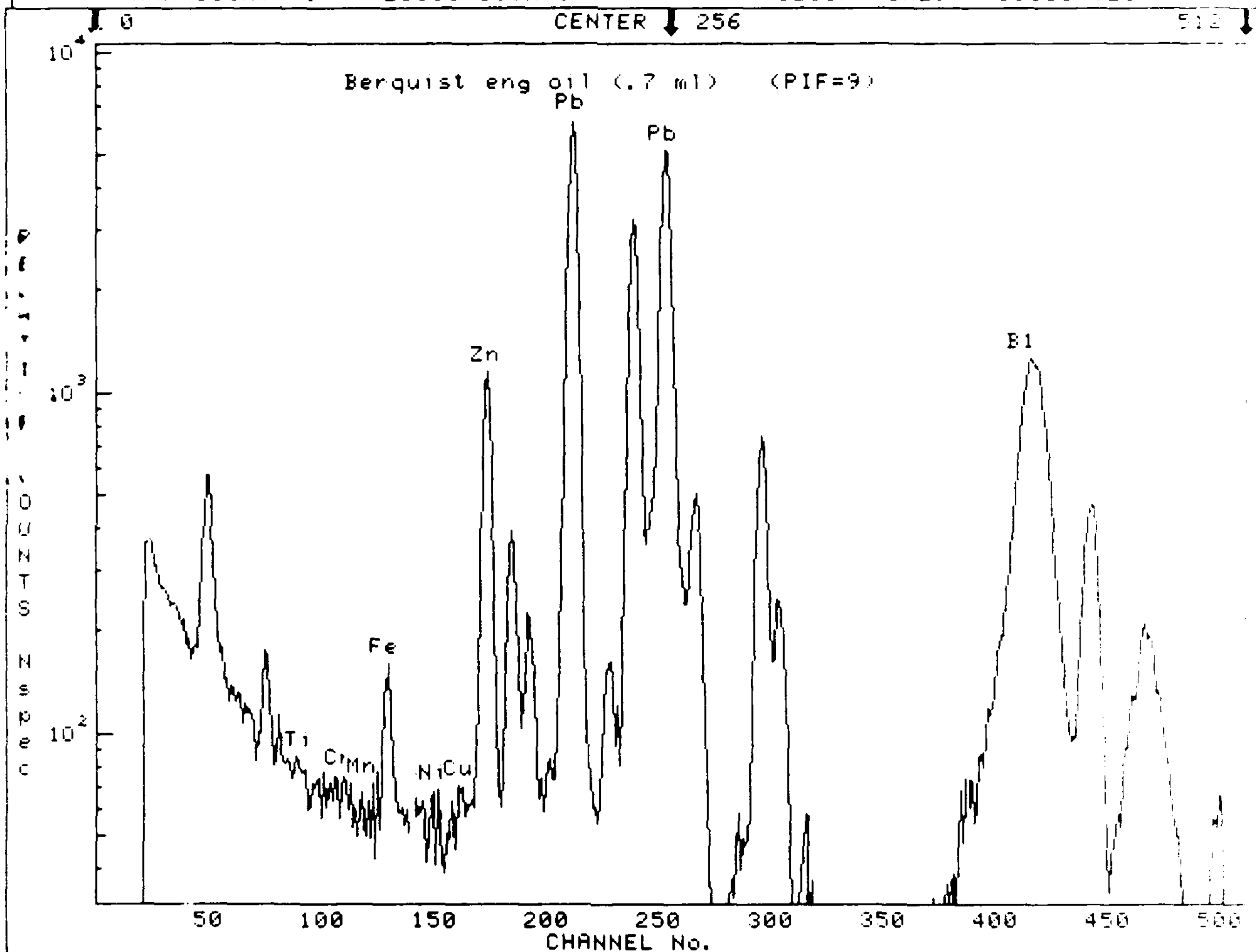
COMMENTS TO DATE

3.5 ml oil, no solvent, 0.45um Tyrann ME filter. In air.

Figure B-7

Berquist eng oil (.7 ml)

	Si(Li)	Cd-109	RunID: Ow-202
STORED UNDER: SPF08B			
SPECTRUM #:	9	OPERATOR:	BClark
CHANNELS :	512	START :	07:28:22
OFFSET :	0	DATE TAPED:	121880
TOTAL COUNT:	160356 COUNTS	COUNT RATE:	16.0 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	20058 COUNTS	CLOCK TIME:	10000 SEC



COMMENTS TO DATE

Millipore (.7 ml filtered) using .8um filter

Figure B-8

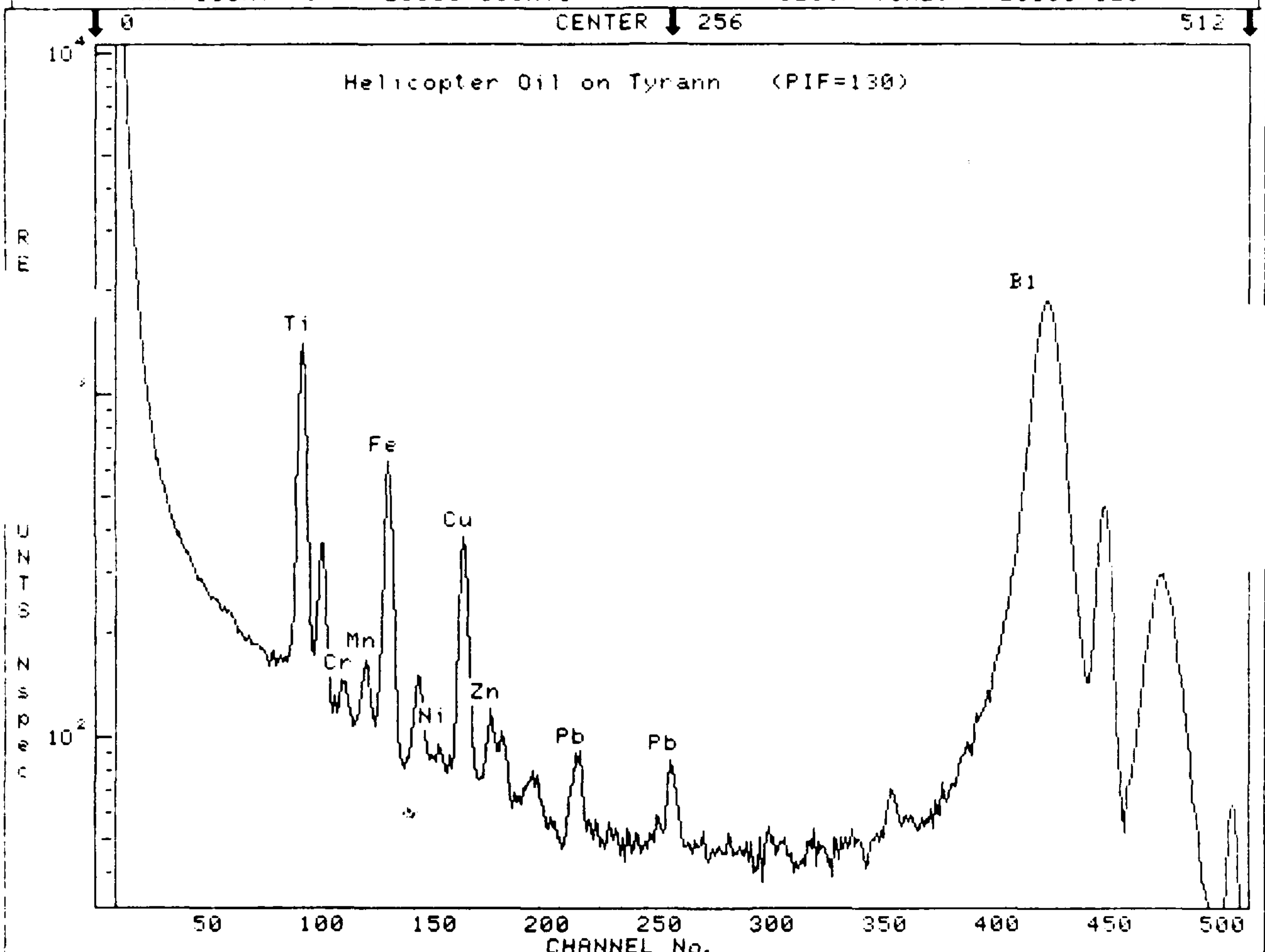
Helicopter Oil on Tyrann 130

Si(Li) Cd-109 RunID: OW-321

STORED UNDER: SPF08B
SPECTRUM #: 130
CHANNELS : 512
OFFSET : 0

OPERATOR: bjc
START : 06:41:18
DATE TAPED: 92881

TOTAL COUNT:	198574 COUNTS	COUNT RATE:	9.9 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	28165 COUNTS	CLOCK TIME:	20000 SEC



COMMENTS TO DATE

- count. 3.5 ml on Tyrann.

Figure B-9

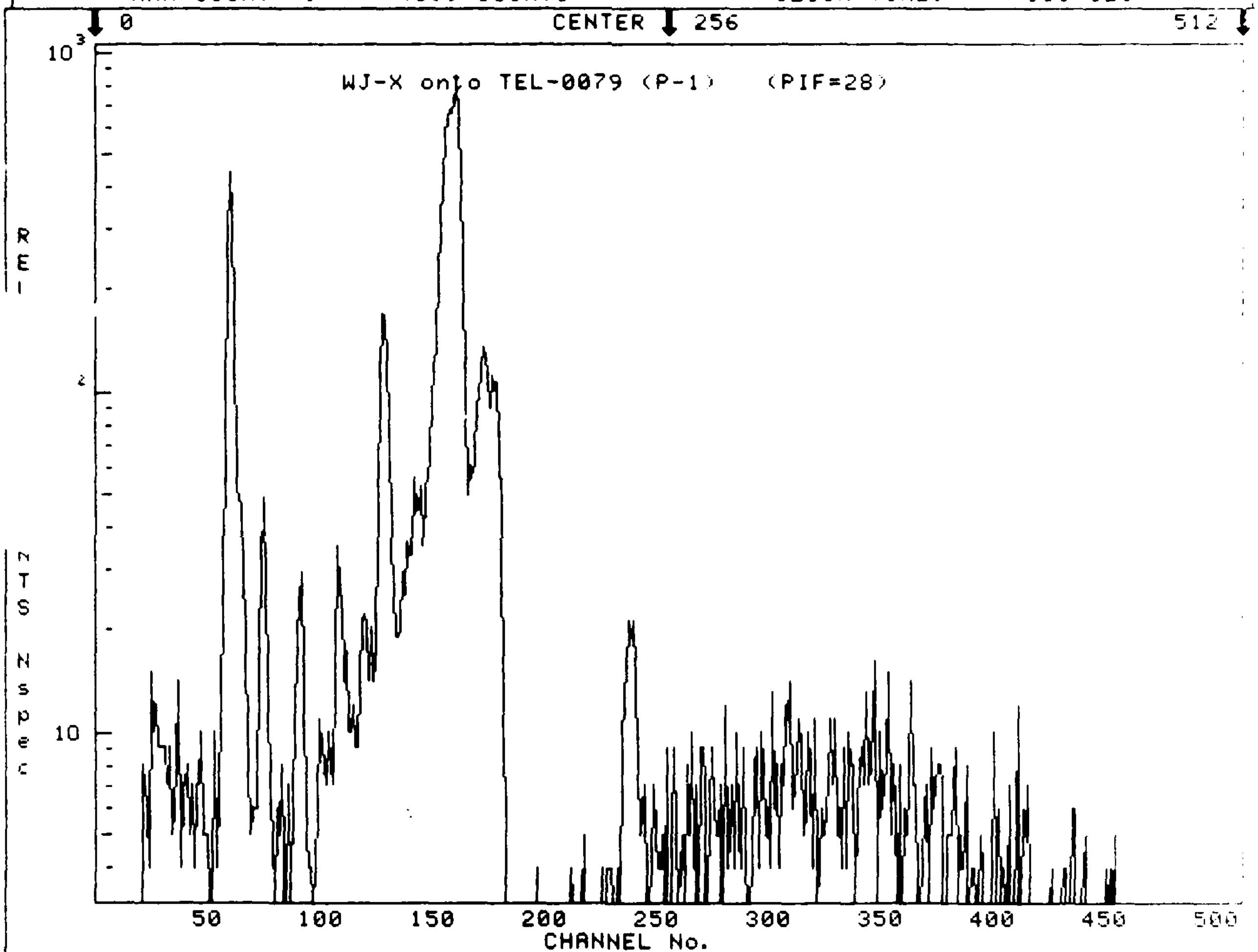
WJ-X onto TEL-0079 (P-1)

Si(Li) Cd-109 RunID: OW 221

STORED UNDER:SPF08B
SPECTRUM #: 28
CHANNELS : 512
OFFSET : 0

OPERATOR: Bcc
START : 00:00:00
DATE TAPED: 000001

TOTAL COUNT:	13101 COUNTS	COUNT RATE:	129.7 CPS
INTEGRATE PEAK:	0 COUNTS	LIVE TIME :	0 SEC
MAX COUNT :	4699 COUNTS	CLOCK TIME:	101 SEC



COMMENTS TO DATE

Prep 1. 25 kV,0.2 mA

Figure B-10

DATE
ILME